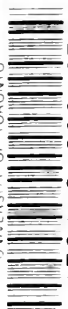
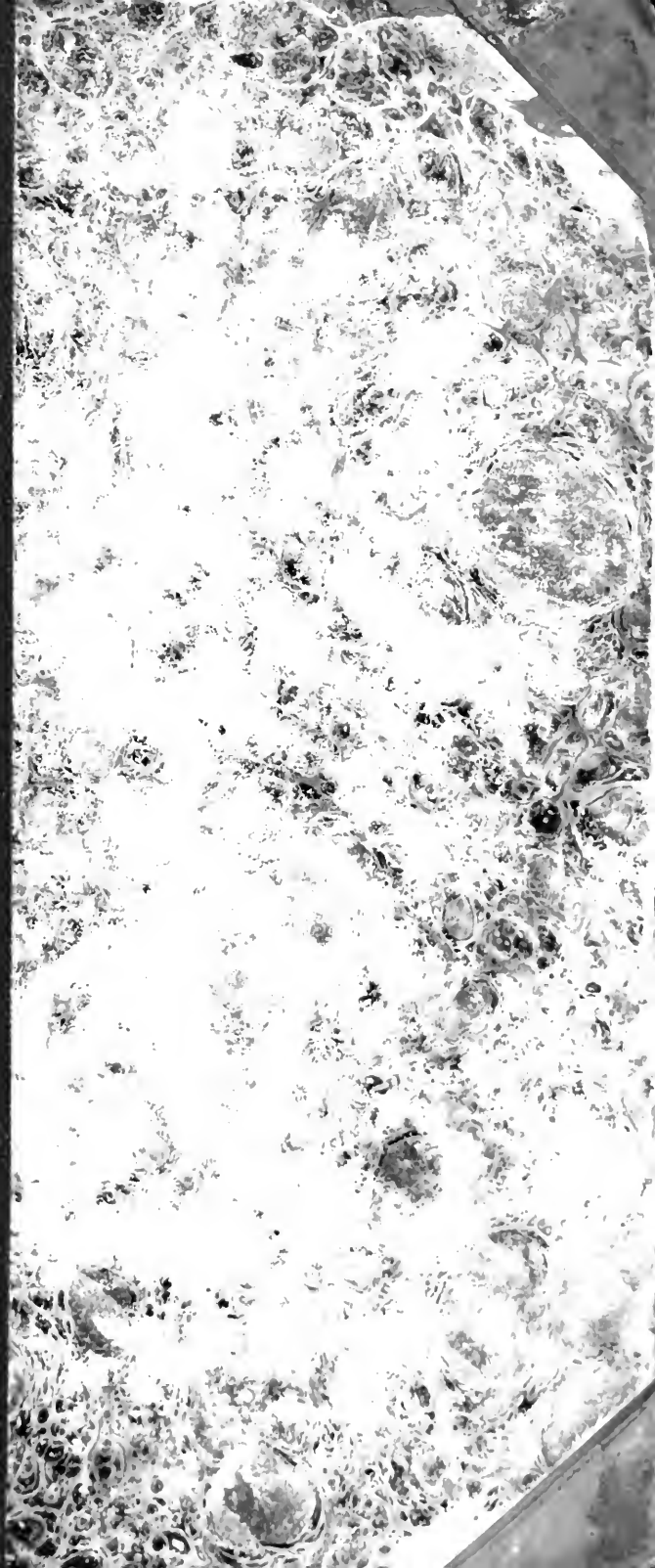


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A

H. J. McLardy

MANUAL

OF

CHEMISTRY;

CONTAINING

THE PRINCIPAL FACTS OF THE SCIENCE: ARRANGED IN THE
ORDER IN WHICH THEY ARE DISCUSSED AND ILLUSTRATED
IN THE LECTURES AT THE ROYAL
INSTITUTION OF GREAT BRITAIN.

BY

WILLIAM THOMAS BRANDE,

*F.R.S., PROF. CHEM. R. I.,
&c. &c. &c.*

THE THIRD EDITION; IN TWO VOLUMES.

VOL. II.

LONDON:

JOHN MURRAY, ALBEMARLE-STREET.

MDCCCXXX.

LONDON :
PRINTED BY WILLIAM CLOWES,
Stamford Street.

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MANUAL OF CHEMISTRY.

CHAPTER V.

OF THE METALS, AND THEIR COMBINATIONS.

Section VIII. MANGANESE.

THE common ore of manganese is the black or peroxide, which is found in considerable abundance, and is of important use in the arts: this metal also occurs in a few animal products, and is not uncommonly discovered in the ashes of vegetables. Particular attention was first directed to the black oxide of manganese by Scheele in 1774, and shortly afterwards Gahn found that it contained a peculiar metal, which he first called *magnesium*, but which was afterwards termed *Manganese*.

In some respects it resembles the metals already described; in others, it is eminently different. Like them, it has a powerful attraction for oxygen, speedily attracting it from air and water; and its oxides are extremely difficult of decomposition: they have, however, nothing in common with alkaline bodies; and manganese, in its highest state of oxydizement, constitutes an acid.

To obtain metallic manganese, the carbonate of manganese may be mixed into a paste with oil, and subjected to heat gradually raised to redness, in a glass or earthen retort. The carbonaceous mixture thus obtained is then rammed into a good crucible, which is filled up with charcoal powder, and subjected for two hours to the strong heat of a wind-furnace: a metallic button is thus obtained, which is manganese, con-

taining a little carbon and silicium, from which it may be freed, according to Dr. John, by fusion with borax in a crucible coated with charcoal; it is doubtful however, as Berzelius has observed, whether in this case it does not contain a little boron.

When the tartrate of manganese and potassa is intensely heated in a wind-furnace it furnishes globules of metallic manganese; and as this salt is easily obtained in a state of purity, its decomposition is perhaps the simplest process for obtaining the pure metal, care being taken to exclude foreign substances derivable from the fuel or from the crucible.

Manganese is a hard gray metal, exhaling a peculiar odour when handled or breathed upon; it is brittle, and has a granular fracture; its specific gravity is 8.013. When pure, it does not affect the magnetic needle. It is best preserved in naphtha; for in the air it soon crumbles down into a black powder, and undergoes the same change in water, with the evolution of hydrogen gas. It may also be conveniently kept in a small glass tube hermetically sealed.

Manganese and Oxygen. — There are four compounds of manganese and oxygen, three of which are oxides, and one an acid.

Protoxide of Manganese is obtained by passing a current of hydrogen over the pure deutoxide or peroxide contained in a porcelain or iron tube, exposed to a heat gradually raised to bright redness: water is formed, and a dingy green powder remains in the tube, which is the protoxide.

It may also be procured by mixing the peroxide with half its weight of muriate of ammonia, and projecting the mixture in successive portions into a red-hot crucible; the product is lixiviated, and the solution of chloride of manganese, thus obtained, is decomposed by the addition of carbonate of potassa; the precipitate is collected, washed, dried, and exposed, out of the contact of air, to an intense heat; or it may be heated in a tube, through which a current of hydrogen is passed.

When the solution of chloride of manganese is decomposed by potassa, a bulky white precipitate falls, which is the *hydrated protoxide* of manganese; it very speedily becomes brown by exposure to air, in consequence of the absorption of

oxygen, and, when collected and washed upon a filter, it becomes a brown powder, which is a hydrate of the deutoxide. The protoxide of manganese is not altered when dry by exposure to air. When heated, it absorbs oxygen, and is converted into deutoxide; and at a temperature of about 600° is said, by Forchammer and Arfwedson, to take fire; but Dr. Turner did not observe this phenomenon. It is readily soluble in the dilute acids, and when put into concentrated sulphuric acid evolves intense heat. Its solutions and salts are nearly colourless when perfectly pure, but they generally acquire a slightly pink hue, probably from the presence of a minute quantity of manganic acid. When ammonia is added to the solutions of this oxide, the whole is not precipitated, but it forms a triple salt, as is the case with magnesia. The equivalent number of manganese deduced from the composition of this oxide is 28, and the oxide is a compound of

1 proportional of manganese	.	.	.	=	28
1 „ oxygen	.	.	.	=	8
					<hr/>
Equivalent of protoxide of manganese	.	.	.	=	36

Deutoxide of Manganese.—When protoxide or carbonate of manganese is exposed for some time to a red heat in an open vessel it absorbs oxygen, and is converted into a deep brown powder. An oxide similarly constituted is also obtained by heating the pure protoxide of manganese till it ceases to give out oxygen, in a platinum crucible. When ammonia is added to the pink solution obtained by triturating a mixture of peroxide of manganese and binoxalate of potassa with water, a precipitate is obtained, which, when well washed and heated red hot, is similar in composition to the above. The characters of this oxide, in respect to solvents, differ with its state of aggregation; but it does not form permanent or definite salts; for such of its acid solutions which are at first red, become colourless when heated, or when exposed to air and light, and deposit peroxide, while a portion of protoxide remains in solution. This oxide consists of

1 proportional of manganese	.	.	.	=	28
1½ „ oxygen	.	.	.	=	12
					<hr/>
Equivalent of deutoxide of manganese	.	.	.	=	40

Or it may be considered as consisting of one proportional of the protoxide, combined with one of the peroxide.

Peroxide of Manganese.—This is the oxide which commonly occurs native, and is resorted to as the source of the other combinations of this metal. In this country it is common in Devonshire, Somersetshire, and Aberdeenshire. It is found in a variety of forms: compact and massive, pulverulent and crystallized. Many of the latter varieties have a gray metallic lustre, and are found acicularly radiated, and in rhomboidal prisms. It also occurs with the native deutoxide, but the exact composition of the native oxides of manganese can scarcely be determined by their external characters. Under the name of *manganese*, this substance is met with in commerce, and is largely consumed in the manufacture of bleaching compounds. In the laboratory, it is resorted to as a cheap and abundant source of oxygen gas, but it sometimes is fraudulently mixed with carbonaceous matter, and then yields carbonic acid. Carbonate of lime, sulphate of baryta, oxide of iron, and other substances, are also frequently associated with this ore. It generally loses considerably in weight, on being dried at a temperature not exceeding 300° ; at a red heat it becomes deutoxide, and, intensely heated in an iron tube, or with a minute quantity of carbonaceous matter, part of it becomes protoxide. It forms no combinations with the acids; but such of them as appear to dissolve it, reduce it to the state of protoxide. Boiled with muriatic acid, chlorine is liberated, in consequence of the decomposition of the acid by the oxygen of the oxide, which is reduced to the state of protoxide, and thus dissolved. Boiled with sulphuric acid, oxygen is evolved, and a sulphate of the protoxide is formed. Nitric acid does not attack it unless some deoxydizing agent be at the same time present. This oxide consists of

1 proportional of manganese	.	.	.	=	28
2 proportionals of oxygen (8×2)	.	.	.	=	16
Equivalent of peroxide of manganese	.	.	.	=	<hr/> 44

The black oxide of manganese is the common source of the protoxide, and of its salts, but it generally contains impurities which require separating. A solution of the pure protoxide may be obtained by digesting the black oxide in muriatic acid

as long as chlorine escapes ; filter the solution, and drop into it a solution of ammonia till the acid is saturated, and the alkali remains in slight excess ; if oxide of iron is present, it is thus precipitated ; excess of ammonia throws down protoxide of manganese ; or it may be more perfectly precipitated by potassa. A chloride of manganese, prepared, as above directed, by heating the peroxide with muriate of ammonia, is also a source of the pure protoxide.

Manganestic Acid.—When peroxide of manganese is heated to redness with nitrate of potassa, a compound is obtained, which, when put into water, furnishes a solution exhibiting various tints of green, purple, and red, and which was therefore called *Chameleon Mineral*. A similar compound is more perfectly obtained by fusing the peroxide with caustic potassa, which furnishes a green substance when the alkali is in excess, but black if the oxide predominate ; the former gives a green, the latter a pink solution, both of which, when duly diluted, exhibit various changes of tint, and ultimately become colourless, with the deposition of a brown powder. It was ascertained by Chevillot and Edwards that this compound could not be obtained in close vessels, but that, air being present, oxygen was absorbed. On evaporating the pink solution, they obtained crystals, which they found to be a true salt of potassa with manganestic acid. This salt, when acted upon by concentrated sulphuric acid, evolves a purple vapour, which condenses in red streaks, and presently decomposes and deposits peroxide. Frommherz succeeded in obtaining manganestic acid as follows :—Two parts of nitrate of baryta are mixed with one of peroxide of manganese, and exposed to a red heat : a green mass is obtained, which is to be reduced to fine powder, mixed with 25 parts of water, and a stream of carbonic acid passed through the mixture, which is kept constantly stirred ; carbonate of baryta is formed, and a deep violet-coloured solution of manganestic acid. When the diffused powder has lost its green colour, the fluid is poured clear off, and boiled for a quarter of an hour to expel excess of carbonic acid, during which a portion of carbonate of baryta and of peroxide of manganese are precipitated : the clear fluid is boiled down to one-fourth its bulk, again left to become clear, and ultimately evaporated to a small bulk : during this evapo-

ration, oxide of manganese is again separated, in consequence of the decomposition of a part of the acid; but the residuary solution forms acicular crystals of hydrated manganic acid, on cooling. All attempts have failed to deprive this acid of water. Its solution has a peculiar astringent taste, possesses considerable bleaching powers, and exhibits a violet colour by transmitted light, but appears of a carmine red by reflected light. It is decomposed by boiling, especially when diluted, and also by exposure to the sun's rays. The exact composition of this acid has scarcely been determined, but it probably consists of one proportional of manganese and four of oxygen. Dr. Forchammer suspects the existence of an intermediate acid in the green chameleon, which he terms *manganeseous acid*, and considers it as a compound of one proportional of manganese and three of oxygen; but the existence of such a compound is not generally admitted. The peculiar green tint obtained by heating compounds of manganese with potassa, is usefully resorted to as a ready means of recognising that metal before the blowpipe.

It is commonly stated that pink solutions, obtained by certain acids from the peroxide, contain the deutoxide; but some experiments, in reference to this subject, made by Mr. Pearsall, in the laboratory of the Royal Institution, render it probable that the appearance of a pink colour is indicative of the presence of manganic acid.

Manganese and Chlorine.—When peroxide of manganese is heated with muriate of ammonia, as above directed (page 2), a solution of *chloride of manganese* is easily obtained, which, if evaporated by a gentle heat, furnishes transparent pinkish crystals, soluble in water and alcohol. The same salt is obtained by dissolving carbonate of manganese in dilute muriatic acid. Exposed, out of the contact of air, to a heat gradually raised to redness, this substance loses water, and forms a beautifully lamellar chloride of manganese, consisting of

1 proportional of manganese	.	.	.	=	28
1 „ chlorine	.	.	.	=	36
Equivalent of chloride of manganese	.			=	64

Heated in the contact of air, chloride of manganese is de-

composed and converted into an oxide, intermediate to the protoxide and peroxide.

A *Perchloride of Manganese* has been described by M. Dumas, formed by adding fused chloride of sodium to a sulphuric solution of manganic acid; the compound passes off in the form of a green vapour, condensable at 0° into an olive coloured liquid. If the vapour be conveyed into a moistened flask it acquires a red tint, and muriatic and manganic acids are generated. The simplest process for preparing it consists in forming a green chameleon mineral by fusing peroxide of manganese with potassa, and pouring dilute sulphuric acid upon it, by which a manganate and sulphate of potassa are obtained. By the affusion of strong sulphuric acid these salts yield a solution of manganic acid, to which small pieces of fused common salt are added, as long as green vapour is evolved. From the phenomena of the decomposition of this chloride, it appears to contain

1 proportional of manganese	.	.	.	= 28
4 proportionals of chlorine (36×4)	.	.	.	= 144
Equivalent of perchloride of manganese	.	.	.	= 172

Ammonio-muriate of Manganese is a soluble and crystallizable salt, not decomposed by excess of ammonia.

Chlorate of Manganese has not been examined.

Iodide of Manganese is a soluble colourless compound. The *iodate* has not been examined.

Fluoride of Manganese is formed, according to Dumas and Wöhler, by mixing the green chameleon-mineral with half its weight of pure fluor spar in fine powder, and decomposing the mixture in a platinum vessel by anhydrous sulphuric acid: a vapour, of a deeper tint than chlorine, is evolved, which acquires a red colour on mixture with atmospheric air, and gives a red solution in water of hydrofluoric and manganic acids. It is decomposed by the contact of glass, fluosilicic acid is formed, and a brown powder deposited, which appears to be anhydrous manganic acid. This fluoride probably consists of one proportional of manganese and four proportionals of fluorine.

Nitrate of Manganese.—Dilute nitric acid readily dissolves protoxide of manganese, and forms a very soluble, deliquescent

less powder, insoluble in water and in alcohol, and not altered by exposure to air. It dissolves in excess of sulphurous acid, and is decomposed by heat. (Berzelius.)

Sulphate of Manganese is formed by dissolving the protoxide or protocarbonate in dilute sulphuric acid, and evaporating: a *protosulphate* is formed, which crystallizes in rhomboidal prisms, and consists, when dry, of

1	proportional of protoxide of manganese	.	.	=	36
1	„ sulphuric acid	.	.	=	40
					<hr/> 76

The crystals contain either four or five proportionals of water.

It is soluble in 2.5 of water, and has a bitter styptic taste: at a bright red heat it gives out oxygen, and sulphurous acid and deutoxide of manganese remain. It may also be obtained by mixing peroxide of manganese into a paste with sulphuric acid, and heating it in a basin nearly to redness: oxygen is evolved, and the dry mass washed with water affords the sulphate. The crystals of this salt have a pink hue, but it appears white when deprived of water of crystallization.

Sulphate of manganese with excess of sulphuric acid forms an uncrystallizable supersulphate. When chlorine is passed through a solution of the neutral sulphate it is decomposed, peroxide is precipitated, supersulphate formed, and muriatic acid is found in the solution.

Ammonio-sulphate of Manganese is a soluble and crystallizable salt. Its crystals contain eight proportionals of water.

Potassa-sulphate of Manganese forms colourless crystals, containing six proportionals of water.

Deutosulphate of Manganese is said to be formed by digesting the deutoxide in sulphuric acid diluted with its bulk of water: a red solution is formed, but the salt cannot be obtained in a neutral or separate state, for the application of heat evolves oxygen, and forms protosulphate. I have already alluded to the doubtful existence of this salt.

Hyposulphate of Manganese.—When peroxide of manganese (previously digested in nitric acid, and thoroughly washed to deprive it of hydrated oxide) is diffused through water, and sulphurous acid passed into it, a neutral hyposulphate of the

protoxide is obtained. It affords a deliquescent salt on evaporation.

Phosphuret of Manganese is of a blue white metallic lustre, and considerably inflammable.

Phosphite and Hypophosphite of Manganese have not been examined.

Phosphate of Manganese is precipitated in the form of a white nearly insoluble powder, by adding phosphate of soda to sulphate of manganese. Berzelius observes, that in analyses this salt is difficultly distinguished from phosphate of lime and phosphate of magnesia. It is, however, decomposed by boiling with caustic potassa, and the oxide assumes a dark colour.

Carburet of Manganese.—When the metal reduced from its oxide is heated with charcoal, it often assumes a lamellated appearance, from combining with that element. Carburet of manganese is also not uncommonly met with in combination with carburet of iron.

Carbonate of Manganese is white, insipid, and insoluble in water. It is precipitated as a hydrate by alkaline carbonates from the protomuriate or protosulphate. When deprived of water, it consists of

1	proportional of protoxide of manganese	.	=	36
1	„ carbonic acid	.	=	22
				<hr/> 58

Borate of Manganese is precipitated in the form of a white powder when solution of borate of soda is mixed with protosulphate of manganese. If the salt of manganese be mixed with a salt of magnesia, borax occasions no precipitate, and the borate is itself soluble in sulphate of magnesia. (Berzelius.)

The salts of manganese containing the protoxide are mostly soluble in water, and the solution often becomes turbid and brown by exposure to air. They are not precipitated by hydriodic acid; they furnish white precipitates with the alkalis, which soon become discoloured by exposure to air; they are precipitated white by ferro-cyanate of potassa, and orange by hydrosulphuret of ammonia. Ammonia only throws down half the oxide, and forms a triple salt with the remainder.

The native peroxide of manganese is used in the laboratory as a source of oxygen, and is largely employed in the prepara-

tion of chlorine, especially by the bleachers. It is used in glass-making, and, when added in excess, gives it a red or violet colour. It is also employed in porcelain painting; and it gives common earthenware a black colour, by being mixed with the materials before they are formed into vessels.

Section IX. IRON.

THE most important native combinations of iron, whence the immense supplies for the arts of life are drawn, are the oxides. Iron is also found combined with sulphur, and with several acids; it is so abundant that there are few fossils free from it. It is also found in some animal and vegetable bodies; and in several mineral waters.

Iron is a metal of a blue-white colour, fusible at a white heat. Its specific gravity is 7.77. It has not been so long known as many of the other metals; it was, however, employed in the time of Moses for cutting instruments. It is extremely ductile, but cannot be hammered out into very thin leaves.

Iron is sometimes found native, and is usually regarded as of meteoric origin, for it is invariably alloyed by a portion of the metal nickel, and a similar alloy is found in *meteoric stones*. *Native Iron* is flexible, cellular, and often contains a green substance of a vitreous appearance. It has been found in Africa, in America, and in Siberia, where a mass of it weighing 1600 lbs. was discovered by Professor Pallas. The mass found in Peru, described by Don Rubin de Celis, weighed 15 tons. In the year 1751, a mass of the same substance was seen to fall from the atmosphere in Croatia. It appeared as a large globe of fire, and is preserved in the imperial museum of Vienna.

Iron and Oxygen.—Exposed to heat and air, iron quickly oxidizes. It unites with oxygen in at least two proportions. When a solution of protosulphate of iron is precipitated by potassa, and the precipitate washed out of the contact of air,

and dried at a red heat, it is black, and nearly pure *protoxide*. In drying, however, oxygen is always absorbed, and a small portion of peroxide is formed.

The oxide, when thus recently precipitated, is sparingly soluble in ammonia, and in carbonated alkalis.

A black oxide of iron may also be obtained by burning iron in oxygen gas: this very beautiful experiment was devised by Dr. Ingenhous, and is best performed by attaching a straight piece of watch spring, wound round with harpsichord wire, to the stopper of an air-jar of oxygen gas; the end of a brimstone match may be attached to the wire, and inflamed at the time of plunging it into the gas; it heats the wire red hot, which then burns and drops in black globules of oxide into the water beneath. A splendid combustion of iron is also effected by placing a small cast iron nail upon a piece of ignited charcoal under a stream of oxygen gas issuing from a blow-pipe.

A similar oxide of iron used to be prepared for pharmaceutical use, by moistening iron filings with a small quantity of water, and exposing them to the air for a day or two; a quantity of black oxide forms, which is separated by washing, and the process repeated till the whole of the metal is thus oxidized. It was called *martial ethiops*. It is black, tasteless, and insoluble in water, but it contains a portion of peroxide.

Perhaps the least exceptionable process for obtaining protoxide of iron consists in passing steam over pure iron wire heated to redness in a porcelain tube. It is dark gray, or nearly black, brittle, and often has some lustre; and after it has been ignited, it is difficultly soluble in the acids; they do, however, dissolve it, and form solutions precisely analogous to those procured by employing metallic iron. This oxide consists of

1	proportional of iron	=	28
1	"	oxygen	=	8
									<hr/>
	Equivalent of protoxide of iron	=	36

When the protosalts of iron are decomposed by caustic potassa a precipitate falls, which, at the first moment, is white, but which immediately becomes gray, then green and blue,

and lastly yellow, in consequence of absorbing oxygen. The white precipitate is probably an *hydrated protoxide of iron*: when boiled with water it becomes black, the hydrate not being a permanent compound at a boiling heat.

When hydrogen gas is passed over protoxide of iron heated to bright redness in a porcelain tube, it is partly decomposed, and a black powder, being a mixture of protoxide and of very finely divided metallic iron, is obtained, which takes fire upon exposure to air. Fused with enamel or other vitrifiable substances, this oxide confers upon them a blue colour.

When protoxide of iron is boiled in nitric acid, and precipitated by ammonia, washed, and dried at a low red heat, it increases in weight, and acquires a brown colour. When a solution of iron in nitromuriatic acid is precipitated by an alkali, a bulky brown *hydrated peroxide of iron* falls, which, when dried, assumes a deeper colour, and is *peroxide of iron*. When sulphate of iron is decomposed at a very high temperature, a red powder remains, which is also the peroxide. In all these cases, although the colour varies, the composition of the oxide is the same; and it has been shown to consist of

1	proportional of iron	= 28
1½	" oxygen	= 12
							—
							40

The hydrated oxides of iron have not been minutely examined, and it is extremely difficult to procure them of uniform composition; indeed, the hydrate of the protoxide cannot be dried without the absorption of oxygen. The yellow hydrate of the peroxide is said to contain between 14 and 15 *per cent.* of water. It is the *Saffron of Mars* of old pharmacy.

It will be observed, that the proportion of oxygen in the protoxide is to that in the peroxide as 1 to 1.5; and, as both these oxides form salts, it will be found that the proto-salts are constituted of one proportional of protoxide, and one of acid, and the persalts of one proportional of peroxide, and one and a half of acid. In the combinations of iron with chlorine, the same relative proportions are followed as in the oxides, but the two sulphurets are respectively constituted of one proportional of iron, and one of sulphur, and one and two.

M. Gay-Lussac (*Ann. de Chim. et Phys.* i., and *Ann. de*

Chim. lxxx.) has detailed some experiments, which he considers as demonstrating the existence of a third definite oxide of iron, intermediate between the above oxides, and composed of iron 100 + oxygen 37.8. Such a compound he thinks is obtained by passing steam for a length of time over red-hot iron, and considers it as differing from the true protoxide: this seems, however, very questionable; and the third oxide is rejected by Berzelius, who only admits the oxides above described.

M. Thenard, in describing the oxides of iron (*Traité*, ii. 75. *édit.* 2^e.), considers the octoëdral and magnetic iron ores as composed of this deutoxide, and does not allow of the existence of native protoxide of iron. In the present state of the question, however, I should feel rather inclined to view this deutoxide as a mixture of the protoxide and peroxide, than as any definite compound, more especially as the analyses of the native magnetic oxides give variable proportions of oxygen.

The *Native Oxides of Iron* constitute a very extensive and important class of metallic ores. They vary in colour, depending upon mere texture in some cases; in others, upon the degree of oxydizement. Some varieties are magnetic, and those which contain least oxygen are attracted by the magnet.

Magnetic Iron Ore is generally black, with a slight metallic lustre. It occurs massive and octoëdral. It is often sufficiently magnetic to take up a needle; its specific gravity is 4.5. It occurs chiefly in primitive countries, and is very abundant at Roslagen in Sweden, where it is manufactured into a bar-iron particularly esteemed for making steel.

Another variety of oxide of iron is called *iron glance*, and *micaceous iron ore*. It is found crystallized of singular beauty, in the isle of Elba; and occasionally among the volcanic products of Vesuvius and the Lipari Islands.

A third variety is *Hæmatite*, or red iron-stone: it occurs in globular and stalactitic masses, having a fibrous and diverging structure. In this country it abounds near Ulverstone in Lancashire; and most of our iron-plate, and wire, is made from it. Sometimes it is of a brown, black, or ochraceous colour.

A fourth variety of oxide of iron is known under the term of

clay-iron-stone, on account of the quantity of argillaceous earth with which it is contaminated. It is found in masses of different shapes and sizes, and sometimes in small rounded nodules like peas. Some of the globular masses are called *atiles*. It is abundant in the coal formations of Shropshire, South Wales, Staffordshire, and Scotland.

Though this is far from the purest iron ore found in this country, it is the principal source of the cast and bar iron, in ordinary use. Its employment is chiefly referable to the coal which accompanies it.

The essential part of the process by which these ores of iron are reduced, consists in decomposing them by the action of charcoal at high temperatures. The argillaceous iron ores are first roasted, and then smelted with limestone and coke; the use of the former being to produce a fusible compound with the clay of the ore, by which the latter is enabled to act upon the oxide, and to reduce it to the metallic state.

Iron and Chlorine unite in two proportions; the *chloride* may be obtained by evaporating *protomuriate of iron* to dryness, and exposing the residuum to a red heat, out of the contact of air. A gray brittle lamellar substance is formed, consisting of

1 proportional of iron	= 28
1 „ chlorine	= 36
						<hr/>
Equivalent of protochloride of iron	= 64

That the chlorine in this *protochloride of iron* is to that in the perchloride as 1 to 1.5, is shown by Dr. Davy in his valuable paper on the chlorides (*Phil. Trans.*, 1812, p. 169), and the equivalent number of iron, as deduced from his analysis, is somewhat above that here adopted. It must be confessed that the anomaly in the oxides and chlorides of iron throws some difficulty in the way of applying to them their equivalent numbers; but as the foundations of chemistry are purely experimental, we must not endeavour to do away that difficulty by a theoretical substitute. There is a difference in the relations of iron to oxygen and chlorine, compared with its relation to sulphur, which does not exist elsewhere; of the cause of this difference we are at present ignorant.

When iron wire is heated in chlorine, it burns with a red

light, and produces a compound which rises in beautiful brown scales. It is the *perchloride of iron*, and consists of

1	proportional of iron	= 28
1½	„	chlorine	= 54
	Equivalent of perchloride of iron	= 82

The chloride and perchloride of iron when dissolved in water produce green and brown solutions, generally termed protomuriate and permuriate of iron. When iron filings are dissolved in muriatic acid, a greenish-brown solution results, which contains a mixture of the protomuriate and permuriate.

Protomuriate of Iron is best obtained by digesting black sulphuret of iron in dilute muriatic acid; sulphuretted hydrogen is evolved, and a green solution obtained, which, filtered and evaporated, yields pale green crystals, very soluble, and of a styptic taste. This salt abundantly absorbs nitric oxide gas; the solution is of a very deep brown colour; when heated, red oxide of iron falls, and a portion of ammonia is formed; a great part of the gas at the same time escapes.

This salt may also be obtained by dissolving iron filings in muriatic acid excluded from air; but the above process is preferable, as the sulphuretted hydrogen prevents any part of the iron passing into the state of permuriate.

By exposure to air, the solution of the green protomuriate passes into the brown permuriate. According to Berzelius, if a solution of the former be exposed for some days to the atmosphere in a tall jar, and a few drops of ammonia be then introduced at different depths, by means of a glass tube, the precipitate near the surface will be green; a little lower, blue; still lower, gray; then of a dirty white; and, at the bottom, quite white, provided the solution has not been so long exposed as to have become oxydized throughout.

By saturating a strong solution of muriate of iron with chlorine, Van Mons obtained a brown liquid, which did not give out the odour of chlorine, and tasted astringent, slightly acid, and sweet. After a time, yellow crystals formed, and chlorine was evolved. The crystals soon deliquesced, and could not be obtained a second time.

Permuriate of Iron is formed by digesting the peroxide in muriatic acid: it dissolves without the evolution of chlorine,

and, when evaporated to dryness, furnishes a reddish-brown deliquescent mass of a very astringent taste, soluble both in water and alcohol. It forms the basis of the *linctura ferri muriatis* of the London *Pharmacopæia*. Permuriate of iron is also formed by exposing the protomuriate to air; and by acting upon it by nitric acid. Exposed to heat, muriatic acid, chlorine, and water, are evolved, chloride of iron sublimes, and a portion of peroxide remains in the retort.

When muriate of ammonia and peroxide of iron are mixed and exposed to heat in a proper subliming vessel, a yellow sublimate is obtained, which is the *ens veneris* and *flores martiales* of old pharmacy—the *ferrum ammoniatum* of the present *Pharmacopæia*; it consists chiefly of muriate of ammonia, with a small but variable proportion of permuriate of iron. If a compound of the muriate of ammonia and of iron be required for pharmaceutical use, it would be best prepared by adding a solution of permuriate of iron to one of muriate of ammonia, and evaporating to dryness.

The *Chlorates of Iron* have not been examined; neither have its combinations with bromine.

Fluorides of Iron.—When iron is digested in hydrofluoric acid, a solution is obtained, which affords small quadrangular tabular crystals; they are colourless, and difficultly soluble in water. Heated rapidly in the air, this salt is decomposed; but if its water of crystallization be slowly and carefully expelled, it then may be fused into a true fluoride of iron.

When hydrated peroxide of iron is dissolved in hydrofluoric acid, it forms a colourless solution, which yields flesh-coloured crystals, slowly soluble in water. Ammonia throws down a yellow precipitate, which is a subfluoride: a triple *fluoride of potassium and iron* is obtained in colourless crystals, when a mixed solution of those fluorides is evaporated.

Iodine and Iron readily form a brown compound, fusible at a red heat, and which, when acted upon by water, forms a *hydriodate* of a green colour.

Iodate of Iron has not been examined.

Nitrates of Iron.—The *nitric acid* dissolves the protoxide and peroxide of iron, and produces a green *protonitrate* and a red *pernitrate*.

Nitric acid, diluted with a very little water, acts violently on iron and peroxidizes it, a vast quantity of gas being at the same time generated, which consists of a mixture of nitrous and nitric oxides; and a solution is formed of a reddish-brown colour, containing *pernitrate* of iron, and affording a brown precipitate to the alkalis. When evaporated, a brown deliquescent mass remains soluble in water and alcohol. It is decomposed at a red heat, and peroxide of iron remains. If this solution be mixed with excess of carbonate of potassa, the precipitate at first thrown down is redissolved by the alkali, and a deep brown liquid obtained, called in our *Pharmacopæia* "*Liquor ferri alkalini*." It has long been known in Germany under the name of "Stahl's alkaline tincture of iron."

If the nitric acid be considerably diluted (sp. gr. 1.16), the action is slow, and very little gas escapes; the solution acquires an olive-brown colour from the nitric oxide which it contains, but exposed to the air it becomes pale green in consequence of the escape of that gas. The alkalis produce a green precipitate in this solution: it cannot be obtained in crystals by the usual process, and passes into pernitrate by exposure to air. It may, however, according to Thomson (*First Principles*, ii. 319), be crystallized by evaporation in an exhausted receiver over sulphuric acid; it then forms transparent rhomboidal crystals of a light green colour, composed of

1 proportional of protoxide of iron	.	.	.	= 36
1 " nitric acid	.	.	.	= 54
7 proportionals of water (9×7)	.	.	.	= 63
				<hr/> 153

The protonitrate of iron is best obtained by dissolving proto-sulphuret of iron in the acid much diluted.

Sulphur and Iron.—There are two sulphurets of iron, the *black* and the *yellow*. The former compound is produced by melting sulphur with iron filings; or rubbing a plate of white-hot iron with a stick of sulphur, which immediately causes it to fuse and run down in the form of sulphuret: this is also the case with steel, but not with good grey cast iron, which is not affected by the contact of sulphur—so that iron and sulphur may be safely fused in a cast iron crucible. (*Ann. de*

Chim, et Phys. xxv. 107.) It is said that a little sulphuret of iron is present in the variety of iron known under the name of *hot short*. It exists in nature under the name of *magnetic pyrites*, which is not found crystallized; it is generally brown, or whitish-yellow, and is not a common mineral. It consists of

1	proportional of iron	= 28
1	„ sulphur	= 16
							<hr/>
	Equivalent of sulphuret of iron	= 44

This compound is best formed artificially by heating filings of iron to bright redness in an earthen crucible, and then dropping upon them pieces of sulphur: the mass presently fuses, and the excess of sulphur is easily driven off. It may also be obtained by adding the alkaline hydrosulphurets to the solutions of the protosalts of iron.

This sulphuret entirely dissolves in the dilute acids, with the evolution of sulphuretted hydrogen gas.

Bisulphuret of Iron is formed, according to Berzelius, when the black sulphuret is well mixed with half its weight of sulphur, and subjected to a high temperature, which, however, must be below redness: a bulky, dark yellow metallic powder is the result, which is not attracted by the magnet, and insoluble in dilute sulphuric and muriatic acid. A similar compound is obtained by passing a current of sulphuretted hydrogen over peroxide of iron at a temperature just below redness. If natural crystals of oxide of iron be subjected to this process, they are converted without change of form into the sulphuret. The sulphuret thus obtained consists of

1	proportional of iron	= 28
2	„ sulphur (16 × 2)	= 32
							<hr/>
	Equivalent of bisulphuret of iron	= 60

Berzelius admits no less than five distinct sulphurets of iron; but some of these are probably mere mixtures of the two definite varieties above described.

Sulphur and iron combine at common temperatures when moisture is present, and a mixture of sulphuret and sulphate of iron is obtained, and oxygen at the same time absorbed. Scheele availed himself of this mixture to analyze atmospheric air. When sulphur and iron filings are mixed in large quan-

tities, and made into a paste with water, they gradually become so hot that ignition ensues: hence the erroneous idea of such mixtures being the cause of volcanic fires and earthquakes.

Under the name of *pyrites*, sulphuret of iron is known as a very abundant natural product.

Common Pyrites is found massive, and crystallized in a variety of forms; its primitive form is the cube. It often occurs in nodules. Its colour is different shades of brass yellow.

That the magnetic pyrites contains just half the proportion of sulphur existing in the common pyrites was first shown by Mr. Hatchett. (*Phil. Trans.*, 1804.) He has also noticed the production of a sulphuret of iron in the waters of the Mere of Diss.

The principal use of pyrites is in the formation of *green vitriol*, for which purpose the ore is gently roasted and exposed to air and moisture. Some varieties are spontaneously decomposed, and furnish this salt, and when in large masses, generate heat enough to become ignited: in this way beds of coal have been set on fire in consequence of the absorption of oxygen by their contained pyrites. Pyrites has also lately been used in the production of sulphuric acid.

Hyposulphite of Protoxide of Iron is obtained by dissolving finely-divided metallic iron in sulphurous acid; a solution is obtained at first brown, but becoming green, and no gas is evolved: it does not crystallize, and is decomposed by exposure to air. When sulphuric or muriatic acids are added to its solution, sulphurous acid is evolved, and sulphur precipitated.

Sulphite of Iron (protosulphite) has not been accurately examined.

Hyposulphate of Protoxide of Iron is formed by mixing a solution of hyposulphate of baryta with protosulphate of iron: the filtered solution furnishes green prismatic crystals, easily soluble, and containing 29.54 *per cent.* of water of crystallization.

Sulphates of Iron.—The sulphuric acid with the protoxide of iron forms a *protosulphate of iron*, which crystallizes in green rhombic prisms, of a styptic taste, soluble in twice their weight

of cold water, and three-fourths of boiling water, and insoluble in alcohol. This salt is called in commerce *copperas* or *green vitriol*, and is often prepared by exposing roasted pyrites to moisture, in which case it is impure. It is usually formed for medicinal and chemical purposes, by dissolving iron filings, or turnings, in dilute sulphuric acid, filtering and evaporating the solution, and setting it aside to crystallize. It is also obtained, perfectly free from persulphate, by acting upon sulphuret of iron by dilute sulphuric acid. This salt in its anhydrous state consists of

1	proportional of protoxide of iron	.	.	.	=	36
1	"	sulphuric acid	.	.	=	40
						<hr/> 76

The crystals include seven, or, according to Mitscherlich, six proportionals of water. Its solution absorbs nitric oxide gas, and acquires a deep brown colour; it also absorbs chlorine, muriatic acid is formed, and the iron becomes peroxidized; so that water is here decomposed.

Exposed to air and moisture, the protosulphate of iron gradually absorbs oxygen, and is partly converted into a persulphate. It may also be converted into persulphate by nitric acid. When heated, it fuses in its water of crystallization, and at a high temperature evolves a mixture of sulphurous and sulphuric acids, peroxide of iron remaining in the vessel: by this process sulphuric acid used formerly to be prepared, and the residue was known under the name of *caput mortuum vitrioli* or *colcothar*. If the green crystals of this salt be exposed to a temperature of about 300°, they lose a portion of water, and crumble down into a white powder, composed of one proportional of dry sulphate, and one of water.

The brown powder which falls when solution of protosulphate of iron is heated in the contact of air is, according to Berzelius, a *sub-persulphate*, composed of 1 proportional of acid, 4 of peroxide, and 6 of water, or 40 acid + 160 peroxide + 54 water = 254.

Protosulphate of Iron and Ammonia is a triple salt, the crystals of which contain six proportionals of water.

Protosulphate of Iron and Potassa is obtained by mixing solutions of proportionals of each of the salts; it is of a very pale tint of green, and the crystals contain six proportionals of water.

Native Green Vitriol is frequently found associated with iron pyrites, being produced by its decomposition: it occurs in several of our coal mines.

Persulphate of Iron is obtained by dissolving the moist red oxide in sulphuric acid; or by adding sulphuric acid to a solution of the sulphate, heating the mixture, and dropping into it nitric acid sufficient to peroxidize the salt. It does not crystallize, but affords, by evaporation, a brown deliquescent mass. It is formed in the mother waters of the sulphate. Its taste is highly astringent; it is soluble in alcohol; and when dry it becomes white; it consists of

1	proportional of peroxide of iron	.	.	.	=	40
$1\frac{1}{2}$	" sulphuric acid	.	.	.	=	60
	Equivalent of persulphate of iron	.	.	.	=	100

When concentrated sulphuric acid is dropped into a strong solution of this persulphate, it throws it down in the form of a white anhydrous powder. This occasionally occurs in sulphuric acid of commerce, and has been mistaken for sulphate of lead.

Ammonio-persulphate of Iron may be obtained in octoëdral crystals, by evaporating a mixed solution of sulphate of ammonia and persulphate of iron. This salt, according to Dr. Forchammer (*Ann. of Phil.* v.) is composed of

Persulphate of iron	41.95
Sulphate of ammonia	12.11
Water	45.94

Persulphate of Iron and Potassa forms octoëdral crystals much resembling alum in form, colour, and taste. These crystals are occasionally found amongst those of common alum, and are a most inconvenient impurity.

Phosphuret of Iron may be formed by dropping phosphorus into a crucible containing red-hot iron wire; it is a brittle grey compound, and acts upon the magnet. Upon the subject of the magnetic qualities of the sulphuret and phosphuret of iron, the reader is referred to Mr. Hatchett's analysis of the magnetical pyrites. (*Phil. Trans.*, 1804.) It may also be procured by the ignition of a mixture of iron filings, phosphoric acid, and charcoal powder; it is very difficultly soluble in the acids. A small portion of this compound is said to be present in all *cold short iron*.

Phosphates of Iron.—These are both insoluble, and may be formed by adding solution of phosphate of soda, to proto-sulphate and persulphate of iron. The *protophosphate* of iron is at first white, but soon becomes of a pale blue colour, and soluble in most of the acids, from which it may again be precipitated by ammonia; the *perphosphate* is white, and not changed by exposure.

These phosphates have been analyzed by Vogel, but his results do not accord with theory (*Ann. of Phil.* xiii. 310), consistently with which the protophosphate should consist of 28 acid + 36 protoxide; and the perphosphate of 42 acid + 40 peroxide.

Native Protophosphate of Iron occurs in the form of a blue earthy powder, and also in prismatic crystals. The former has sometimes improperly been termed *Native Prussian Blue*, and has been found in alluvial soil: the latter occurs with iron pyrites in Cornwall. The blue crystallized variety analyzed by Stromeyer (*Untersuchungen*, i. 274) afforded

Phosphoric acid	2.73
Protoxide of iron	3.64
Water	2.42
						<hr/> 8.79

These numbers are nearly equivalent to

1 proportional of protoxide of iron	.	.	.	= 36
1 " phosphoric acid	.	.	.	= 28
3 proportionals of water (9 × 3)	.	.	.	= 27
				<hr/> 91

Iron and Carbon.—The different kinds of cast iron and of steel contain more or less carbon, which materially affects their properties. The substance termed *Plumbago*, *Graphite*, or *Black Lead*, is generally regarded as a true *carburet of iron*: this is not an uncommon mineral, though rarely found of sufficient purity for the manufacture of pencils: at Borrodale in Cumberland, where it occurs particularly pure, it is in imbedded masses in slate and grauwacke: the coarser kinds and the dust are melted with sulphur for common carpenters' pencils: it is sometimes used in the manufacture of crucibles, and it forms an ingredient in compositions for covering cast-iron,

and for diminishing friction in machines. According to Messrs. Allen and Pepys, it consists of

$$\begin{array}{r} 95 \text{ carbon} \\ 5 \text{ iron} \\ \hline 100 \end{array}$$

Plumbago is infusible, and burns with great difficulty; its composition was ascertained by the above-mentioned chemists, by exposing it in the apparatus used for burning the diamond, to a current of oxygen at a red heat, and ascertaining the quantity of carbonic acid and of oxide of iron thus produced.

It may here be observed, that considerable difficulty attends the accurate analysis of artificial compounds of carbon and iron, in estimating the proportion of the former; this has generally been indirectly effected by ascertaining the quantity of iron, and considering the loss of weight as carbon, a method obviously objectionable. If the action of dilute sulphuric acid be resorted to, a portion of carbon is carried off by hydrogen; the same is the case with muriatic acid; and if nitric acid be used, some carbonic acid may be formed, and artificial tannin is produced.

Carbonates of Iron.—Carbonic acid may be combined with the protoxide of iron, by adding carbonate of potassa to sulphate of iron; a white or greenish precipitate of *protocarbonate of iron* falls, which, exposed to air, becomes brown, and evolves carbonic acid. Solution of bicarbonate of potassa occasions a white precipitate with sulphate of iron, part of which is redissolved on adding excess of the carbonated alkali. When carbonic acid in aqueous solution is digested with iron filings, a colourless solution of the protocarbonate is obtained: it is not an uncommon ingredient in mineral waters. The protocarbonate of iron consists of

$$\begin{array}{rcl} 1 \text{ proportional of protoxide of iron} & . & . & . & = 36 \\ 1 \text{ ,, carbonic acid} & . & . & . & = 22 \\ & & & & \hline & & & & 58 \end{array}$$

Spathose Iron Ore is a native carbonate of iron, containing a little manganese and carbonate of lime. It occurs in Germany, and in some parts of Cornwall, crystallized in imperfect rhomboids. Its colour is yellowish, or brownish-grey. A

specimen of this mineral from Eulenhoh in Bareuth, analyzed by Bucholtz (*Gehlen's Journal*, i. 231), contained

Carbonic acid	36
Protoxide of iron	59
Lime	3
Water	2
					<hr/>
					100

These components indicate the above mineral to consist essentially of protocarbonate of iron, composed as above.

A *percarbonate of iron* cannot be obtained in a separate state; for the protocarbonate, whilst drying, exposed to air, loses carbonic acid, and becomes peroxide. When bicarbonated alkalis are digested with recently precipitated peroxide of iron, triple salts are formed.

Ferrocyanates of Iron.—When hydrocyanate of potassa is added to the solutions of salts of iron, it occasions a white or bluish-white precipitate in those containing the protoxide, and a blue precipitate in those containing the peroxide. The former precipitate is probably a ferrocyanate of iron, containing the protoxide; the latter, a ferrocyanate, containing the peroxide, and which has been long known under the name of *Prussian Blue*.

Prussian blue is usually prepared by the following process: Equal parts of carbonate of potassa and some animal substance, such as dried blood, or horn shavings, are heated red-hot, in a crucible, for half an hour, and six or eight parts of water are poured upon the mixture when it has quite cooled. The solution, which used to be called *lixivium sanguinis*, is filtered and found to contain *hydrocyanate of potassa*, along with carbonate of potassa, and some other products. It is mixed with a solution containing two parts of alum and one of sulphate of iron; a precipitate falls, at first of a dingy green hue, but which, by copious washings with very dilute muriatic acid, acquires a fine blue tint, and is called *Prussian Blue*, having been discovered by Diesbach, a colour-maker of Berlin, in 1710. The first description of the mode of preparing it is given by Woodward in the *Phil. Trans.* for 1724.

In this process the animal matter is decomposed, and resolved into a variety of products arising from the re-union of its ultimate component parts. The matter remaining in the

crucible contains cyanuret of potassium ; and when acted upon by water, hydrocyanate of potassa, with a little carbonic acid and ammonia, is formed in consequence of the decomposition of a portion of the water ; and consequently the principal salts contained in the washings of the black matter remaining in the crucible are carbonate and hydrocyanate of potassa, which, when added to a solution of sulphate of iron, form a precipitate of carbonate and ferrocyanate of iron ; the former is removed by the dilute muriatic acid. The aluminous earth of the alum gives a *body* to the precipitate, which improves it as a pigment.

The above seems to be the simplest view of the formation and composition of Prussian blue ; a variety of other opinions respecting its nature have been entertained, but they require further experimental verification.

Pure Prussian blue, obtained by adding ferrocyanate of potassa to solution of persulphate of iron, is a tasteless substance, insoluble in water * and alcohol. It is not acted upon by dilute nitric, sulphuric, or muriatic acids, which renders it extremely improbable that it should be a hydrocyanate of iron, and strengthens the opinion of Mr. Porrett, that it is a *Ferrocyanate*, or a compound of peroxide of iron with the peculiar acid mentioned below, and containing hydrogen, oxygen, iron, and cyanogen.

Subjected to distillation, *per se*, Prussian blue yields water, hydrocyanate of ammonia, carbonic acid, and other gases (*Ann. of Philos.* Sept. 1820). It may be heated to 300 without decomposition ; at higher temperatures it burns like tinder, and leaves a residue of oxide of iron. When dried and exposed to humid air it rapidly absorbs moisture. According to Robiquet (*Ann. de Chim. et Phys.* xii.), sulphuric acid renders Prussian blue white, but the colour is restored on dilution ; this, he thinks, depends upon the abstraction of water, since no traces of prussic acid or of iron are discoverable in the concentrated acid thus employed. Kept in contact of iron-filings and water, or subjected to the action of sulphuretted hydrogen, Prussian blue is rendered white, apparently in consequence of the deoxidizement of the iron, for the blue colour returns upon exposing it to air.

* Under certain states of recent precipitation, however, water does dissolve a portion.

Ferrocyanate of Potassa.—When Prussian blue is boiled with potassa it is decomposed; it loses its blue colour, oxide of iron is separated, and on filtering and evaporating the solution, a triple salt is obtained, consisting of hydrocyanic acid, potassa, and oxide of iron; this has been called *triple prussiate of potassa*, and *ferrocyanate of potassa*. It is best formed by adding powdered Prussian blue (previously heated with a dilute sulphuric acid composed of one part of acid and five of water, and afterwards washed) to a hot solution of potassa, as long as its colour is destroyed. This salt forms permanent yellow crystals, of a specific gravity of 1.83: they are more soluble in hot than cold water, insoluble in alcohol, and of a cooling saline taste. Dr. Ure states, that water at 60° takes up about one-third, and at 212° its own weight of this salt. The large crystals have a peculiar toughness, and the thin ones are somewhat flexible and elastic: their forms have been described by Mr. Levy and Mr. Brooke. (*Quarterly Journal*, xv. 288; *Ann. of Phil. N.S.* vi. 41.) Boiled with dilute sulphuric or muriatic acids, hydrocyanic acid is given out, and a white precipitate formed similar to that which the salt produces in a solution of protosulphate of iron. When moderately heated it loses its colour, and crumbles down into a white powder, parting with about 13 per cent. of water of crystallization. The crystals retain their figure till upon the verge of ignition. It is decomposed in a retort at a red heat, hydrocyanic acid and ammonia are evolved, and the residue consists of charcoal, potassa, and iron.

Neither sulphuretted hydrogen, the hydrosulphurets, nor tincture of galls, produce any change in solutions of this salt. Red oxide of mercury decomposes it at a moderate heat, peroxide of iron and metallic mercury are precipitated, and cyanuret of mercury formed; so that the iron is peroxidized at the expense of a portion of the oxide of mercury.

This salt in crystals consists, according to Dr. Ure, of

Water of crystallization	13.
Potassa	41.68
Ferrocyanic acid	45.32
						<hr/> 100

According to Dr. Ure (*Dictionary*, p. 92, 2d edit.) crystal-

lized ferrocyanate of potassa is manufactured upon the large scale, for the use chiefly of calico printers and dyers, as follows:—

“ Into an egg-shaped iron pot, brought to moderate ignition, project a mixture of good pearl-ash and dry animal matters, of which hoofs and horns are best, in the proportion of two parts of the former to five of the latter. Stir them well with a flat iron paddle. The mixture, as it calcines, will gradually assume a pasty form, during which transition it must be tossed about with much manual labour and dexterity. When the conversion into a chemical compound is seen to be completed by the cessation of the fetid animal vapours, remove the pasty mass with an iron ladle. If this be thrown, while hot, into water, some of the prussic acid will be converted into ammonia, and of course the usual product diminished. Allow it to cool, dissolve it in water, clarify the solution by filtration or subsidence, evaporate, and, on cooling, yellow crystals of the ferroproussiate of potash will form. Separate these, redissolve them in hot water, and by allowing the solution to cool very slowly, larger and very regular crystals may be had.”

When ferrocyanate of potassa is exposed to a red heat in a platinum crucible, a brown mass is obtained, which, washed with water, deposits a grey cyanuret of platinum. The aqueous solution furnishes, on evaporation, hydrocyanate of potassa and a large quantity of transparent colourless prismatic crystals.—Thenard, *Traité*, 2d edit., iii. 528.

Mr. Porrett (*Phil. Trans.* 1814) considers the ferrocyanates as compounds of the respective bases, with an acid consisting of the elements of the hydrocyanic acid united to the protoxide of iron. This acid he terms *ferrochyazic acid*, derived from the initial letters of carbon, hydrogen, and azote. He obtained this acid dissolved in water, by adding to a solution of ferrocyanate of baryta just sulphuric acid enough to precipitate the baryta. In this state it has a pale yellow colour, no smell, and is decomposed by a gentle heat or strong light, in which case hydrocyanic acid is formed, and white hydrocyanate of iron is deposited, which becomes blue by exposure. To obtain crystallized ferrochyazic acid, Mr. Porrett recommends the following process. Dissolve 58 grains of crystallized tartaric acid in alcohol, and pour the solution into a phial con-

taining 50 grains of ferrocyanate of potassa dissolved in 3 drachms of warm water; by these means, the potassa is precipitated in the state of supertartrate, and the ferrochyzic acid remains dissolved in the alcohol, from which it may be obtained by careful evaporation in small cubic crystals. (*Ann. of Philos.* Sept. 1818.) Gay-Lussac, observing the production of the ferrocyanate of potassa by adding protoxide of iron to hydrocyanate of potassa, supposes that a portion of the hydrocyanic acid is decomposed by the oxide, giving rise to a compound of cyanuret of iron with hydrocyanate of potassa.

Much diversity of opinion, however, still exists respecting the nature of Prussian blue, and the ferrocyanate of potassa. It has already been stated that Prussian blue is probably a ferrocyanate of the peroxide of iron, and that the ferrocyanate of the protoxide of iron when perfectly pure is white. Mr. Porrett considered the ferrocyanic acid as composed of one proportional of iron, one of hydrocyanic acid, and two of carbon; but it has been shown by Robiquet, that its elements are in such relative proportions as to form cyanuret of iron and hydrocyanic acid, and that it probably consists of

1	proportional of cyanuret of iron	.	.	=	54
2	„ hydrocyanic acid (27 × 2)			=	54
					<hr/> 108

Its ultimate elements, therefore, are

1	proportional of iron	
2	"	hydrogen
3	"	nitrogen
6	"	carbon

} = 3 of cyanogen

And the anhydrous ferrocyanate of potassa would consist of

1	proportional of ferrocyanic acid	.	.	=	108
2	" potassa (48 X 2)	.	.	=	96
					<hr/>
					204

There is still more difficulty in determining the relative proportions of the elements of Prussian blue, but it is probably a compound of

1 proportional of peroxide of iron	.	.	.	=	40
1½ „ ferrocyanic acid	.	.	.	=	162
					<hr/> 202

The following Table shows the colours of the precipitates occasioned by solution of ferrocyanate of potassa, in different metallic solutions:—

<i>METAL.</i>	<i>SOLUTION.</i>	<i>PRECIPITATE.</i>
MANGANESE .	Neutral protomuriate	White
IRON . .	Neutral protosulphate	White or pale blue
Ditto . .	Permuriate	Prussian blue
ZINC . .	Muriate	Yellowish white
TIN - . .	Acid protomuriate	White, then yellow and bluish
Ditto . .	Acid permuriate	Pale yellow
CADMIUM . .	Muriate	White
COPPER . .	Protomuriate	Lilac
Ditto . .	Pernitrate	Deep brown
LEAD . .	Nitrate	White
ANTIMONY . .	Tartrate of antimony and potassa	0
BISMUTH . .	Tartrate of bismuth and potassa	0
COBALT . .	Muriate	Pale green
URANIUM . .	Sulphate	Deep brown
TITANIUM . .	Acid muriate	Deep blue (from acid)
Ditto . .	Neutral sulphate	Sap green
CERIUM . .		White
TELLURIUM . .		
ARSENIC . .	White oxide	
Ditto . .	Arsenic acid	
NICKEL . .	Sulphate	Grey
MERCURY . .	Acid nitrate	Greenish white
Ditto . .	Acid pernitrate	Ditto
Ditto . .	Corrosive sublimate	White
RHODIUM . .		0
PALLADIUM . .	Muriate	Olive
SILVER . .	Nitrate	Cream colour
GOLD . .	Muriate	0
PLATINUM . .	Ditto	Yellow

All the above precipitates appear to be ferrocyanates, for when treated with solution of potassa, a ferrocyanate of potassa is obtained.

Ferrocyanate of Soda is obtained by treating Prussian blue with solution of pure soda. It forms four-sided prisms, terminated by dihedral summits, which effloresce, and lose in a warm atmosphere about 37 *per cent.* of water. At 55° they are soluble in 4.5 of water. They are soluble in alcohol.

Ferrocyanate of Lime is formed by digesting Prussian blue in lime water, or by boiling a mixture of Prussian blue, lime, and water. It crystallizes with difficulty in small grains.

Ferrocyanate of Baryta is formed in the same way as the preceding salts. It crystallizes in yellow rhomboidal prisms, soluble in 2000 of cold and in 100 of boiling water. They consist, according to Mr. Porrett, of

Ferrocyanic acid	41.5
Baryta	47.5
Water	11.0
						<hr/> 100.

Ferrocyanates of Strontia and of *Magnesia* have also been obtained.

Ferrocyanuret of Potassium.—When chlorine is passed through a solution of ferrocyanate of potassa till it ceases to precipitate the persalts of iron, and the fluid then filtered and slowly evaporated, it furnishes small crystals, which, purified by a second solution, assume a ruby-red colour; they require 38 parts of cold water for solution, and are nearly insoluble in alcohol. This salt, although it occasions no change in solutions of iron containing the peroxide only, is a most delicate test of the protoxide of that metal. According to Gmelin, this salt is a cyanuret of potassium and iron, consisting of

Potassium	35.68
Iron	16.48
Cyanogen	47.84
						<hr/> 100.

Similar salts of ammonia, soda, lime, and baryta, may be obtained by treating the solutions of their respective ferrocyanates in the same way, care being taken to avoid, in all cases, excess of chlorine, which re-acts upon the salt. The solution

of the ferrocyanuret of potassium throws down the following metals, of the annexed colours :—

Titanium	.	Brownish yellow.
Uranium	.	Reddish brown.
Manganese	.	Brownish grey.
Cobalt	.	Dark red-brown.
Nickel	.	Yellowish brown.
Copper	.	Dirty yellow-brown.
Silver	.	Orange yellow.
Mercury	.	Yellow (both oxides).
Tin	.	White.
Zinc	.	Orange.
Bismuth	.	Yellow brown.

Lead affords at first no precipitate, but after a time reddish-brown crystals separate. By decomposing these crystals by sulphuric acid, a peculiar ferrocyanic acid was obtained, of a red colour.

Protoborate of Iron is an insoluble powder, obtained by adding a solution of borate of soda to one of protosulphate of iron.

Perborate of Iron is of a yellow colour, and insoluble. It is formed by adding borate of soda to persulphate of iron: it is vitrifiable at a high heat. When hydrogen is passed over borate of iron, heated red hot in a porcelain tube, it is converted into a *boruret of iron*, consisting of 77.43 iron, 22.57 boron. (Lassaigne.)

The salts of iron are mostly soluble in water, and the solution is reddish brown, or becomes so by exposure to air. They afford a blue precipitate with ferrocyanate of potassa; and a black precipitate with hydrosulphuret of ammonia. Infusion of gall-nuts produces a black or deep purple precipitate. The hydriodic acid occasions no change.

Soda-muriate of gold is an extremely delicate test of the protosalts of iron. A grain of protosulphate of iron, with an equal weight of soda, dissolved in four pints of water, produces a precipitate, gradually becoming purple on the addition of a drop of solution of muriate of gold. Without the soda, the effect did not appear in less than three days. (Ficinus, *Quarterly Journal*, xv. 382.)

Of the alloys of iron, *tin-plate* is the only one of consequence. It is made by dipping clean iron plates into melted tin. The process is described at length by Mr. Parkes:

(*Quarterly Journal*, vol. viii. 141.) When tin-plate is washed over with a weak acid, the crystalline texture of the tin becomes beautifully evident, forming an appearance which has been called *moiré métallique*.—*Quarterly Journal of Science*, vol. v. p. 368.

It has already been stated that the nodular argillaceous iron ore is that which is chiefly resorted to in this country as the source of the metal; the following is an outline of the process of reduction, abridged from the detailed account given in Messrs. Aikins' *Dictionary*, and in the *Supplement to the Encyclopædia Britannica*, to which the reader is referred:—

“The first process that the ore undergoes after it has been broken into small pieces, is *roasting*. This is performed as follows:—Upon an oblong piece of firm and level ground is laid a bed of small coal, from four to eight inches thick; upon this is placed a stratum of ironstone, from eighteen inches to two feet thick: the upper surface of which is rendered more compact by filling up the interstices with smaller pieces. Upon this rests a layer of small coal not more than two inches thick, and on this, as a base, is reared a gradually diminishing pile of ore; finally, the whole external surface receives a complete covering of small coals and coal dust. The pile is kindled by applying burning coals to the lower stratum. The breadth of the pile at the bottom varies from ten to sixteen feet, the usual height is about five feet, and the length varies from thirty feet to sixty yards. When the coals are consumed, the pile gradually cools, and in eight or ten days may be wheeled away to the furnace.

“The ore, if well roasted, will now be of a reddish brown colour, of diminished specific gravity, and will have become magnetical; the sulphur, water, inflammable matter, and carbonic acid that it originally contained, will have been dissipated, and it is now ready to be smelted.

“The furnace resembles externally a truncated quadrilateral pyramid of considerable height in proportion to its thickness, it is built of the strongest masonry, with contrivances to obviate the danger of its cracking by the expansion that takes place when it is heated. The interior of the furnace consists of the five following parts, reckoning from the bottom upwards.

“First, the *hearth*, composed of a single block of quartz grit about two feet square : upon this is erected what in France and Germany is called the *crucible*, which is a four-sided cavity six feet six inches high, slightly enlarging upwards so as to be two feet six inches square at the top : the part above, called the *boshes*, is in the shape of a funnel or inverted cone, eight feet in perpendicular height, and twelve feet in diameter at the top ; this terminates in the *cavity* of the furnace, which is of a conical figure, thirty feet high, and three feet diameter at the top ; from this part it enlarges into a funnel-shaped *chimney*, about eight feet high, and sixteen in diameter at its mouth. About two feet above the hearth is a round aperture, called the *Tuyere*, made in one of the sides of the crucible to admit the extremity of the blast pipe, through which the air in a high state of compression is forced into the furnace ; and at the bottom of the crucible is an aperture, through which the scoræ and melted metal are from time to time discharged. A furnace of this construction, if it meets with no accident, may be kept in constant work for three years or more without requiring any repairs.

“The furnace is charged at the chimney, by regular intervals, with coke, iron ore, and limestone, in the proportion of about four of the first, three and one-third of the second, and one of the third, by weight, care being taken so to regulate the frequency of the charges, as that the furnace shall be always full nearly to the top of the great cavity. The density of the blast and the form of the discharging pipe are ordered so that the chief focus of heat is about the bottom of the boshes ; hence the ore has to descend about thirty-eight feet perpendicular, before it arrives at the place where the fusion is effected. This does not happen in less than forty-eight hours ; so that the ore is all this time in a state of cementation at a high temperature, in contact with the burning fuel, and, in consequence, is almost saturated with carbon when it reaches the hottest part of the furnace. Being arrived at this place, the limestone flux, and the earthy particles of the coke and ore run down into a slag ; the iron is also melted, and more or less decarbonized, and in part oxydated by the blast, inversely, according to the proportion of fuel with which it is mixed. The fluid mass soon sinks down below the influence of the

blast, and while it remains in quiet at the bottom of the furnace, the globules of iron are precipitated from the slag, and occupy the lowest place, while the covering of scorïæ thus interposed between the metal and that portion of the blast which is reflected downwards, prevents it from suffering any further loss of carbon. In proportion as the melted matter accumulates, the slag being the uppermost, flows out at the aperture made for this purpose, and the iron is let out at regular intervals into furrows made in sand, where it forms what is called *pig-iron*, or into a large reservoir, whence it is poured by means of ladles into moulds, forming all the various articles of cast iron ware.

“The following are some of the circumstances in the smelting which influence the quality of the produce. Much depends on the fuel: if the coke is not perfectly made, but retains bitumen, the whole mass cakes in the upper part of the furnace, and, instead of descending regularly to the focus of heat, falls down at irregular intervals, so that part of the metal is detained too long before the blast, and decarbonized and oxydated, while other portions pass so rapidly through the furnace as never to be thoroughly reduced; hence the amount of the produce is diminished, and its quality deteriorated. Nor is it of less importance that the coke should be dry when put into the furnace. The proportion of fuel should also be adapted to the richness of the ore, so that there may be sufficient both to keep up the necessary degree of heat as well as to carbonize the metal: hence, as the charges of ore and fuel are always proportioned by measure, if an ore somewhat richer than usual happens accidentally to be employed without a corresponding addition of fuel, the produce, though somewhat increased in quantity, will be more than equivalently reduced in quality. Another circumstance that the manufacturer must carefully attend to, is the proper choice of ore with regard to fusibility; for, as it is not only requisite that the iron should be melted, but also highly carbonized, and as coke gives off its carbon more difficultly than charcoal, a very fusible ore would melt long before it arrived at the focus of the furnace, and passing rapidly through, would reach the hearth without having had time to imbibe the proper quantity of carbon. Hence it is, that the rich *hematites*, although they afford an excellent qua-

lity of iron when smelted with charcoal, produce nothing but white iron when treated in the coke-furnace; while, on the other hand, *argillaceous ironstone* being much more refractory, does not melt till it comes into the very hottest part of the furnace, and therefore has had full time to absorb the desirable quantity of carbon. Another thing to be attended to, is the proper regulation of the blast, and this depends upon its dryness, its temperature, its compression, and its direction. The dryness and temperature appear to be principally governed by the season of the year. The dryer and colder the air is, the greater will be its effect on the combustion; and it is found that the produce of iron during the summer months, is inferior in quantity and quality to that which is manufactured in the winter: a clear, dry, and severe frost is the most favourable period in every respect for the working of the furnace, and a change to snow or rain is followed by a corresponding deterioration. The higher the temperature of the blast when it is delivered into the furnace, the smaller will be the quantity of oxygen contained in every cubic foot, and, of course, the vigour of the combustion. Nor is the force of the blast and its direction a subject of less importance; it is obvious, that in proportion as the charge descends, the carbonaceous matter is continually diminishing; hence the proper situation for the focus of the blast is that part of the furnace, where, when the ore shall have arrived, it will be fully carbonized and surrounded with a sufficient quantity of fuel to excite an intense heat, and absorb nearly the whole of the oxygen of the air, and thus prevent it from either oxydating the iron, or carrying off the carbon with which it may be combined. This precise situation, in a furnace properly constructed, will be found to be just within the expansion of the boshes; but as this is more than four feet above the tuyere hole, the blast must be delivered with great velocity, and in a direction somewhat slanting upwards, in order that it may be reflected by the opposite wall of the crucible, and arrive at its proper place without undergoing any material decomposition. When the blast enters too rapidly, and in too concentrated a state, it renders the line of its passage, before it is reflected, so cool, that the descending slag which comes within its influence is suddenly solidified, and blown into a tube, reaching perhaps

half way across the crucible, through which the blast continues to rush; and in consequence of this protection, is conveyed with greater precision, and in a less decomposed state, into the upper part of the furnace. If, after this, the compression of the air is somewhat diminished, the tube still remains firm, often for days together, and the furnace works in the best manner. But, on the other hand, when too loose and soft, a blast is admitted, and more especially if it is charged with moisture, it is unable to reach the top of the crucible without being decomposed, and the reflection which it undergoes from the wall of the crucible, weakens and disperses it to such a degree, that the combustion which ought to take place within the boshes, now occupies the whole upper part of the crucible: in consequence of this, the tube of scoriæ is presently burnt away, the iron, almost as fast as it is melted, is ignited and oxydized, the tuyere hole glows, like the sun, with an intensely vivid white light; the scoriæ, from being yellowish white streaked with blue, becomes green, brown, and finally black, nearly the whole of the iron in the state of oxyde being taken up by it; the blocks of refractory gritstone, with which the lower part of the furnace is lined, are worn into great holes, and in the space of a few hours prodigious damage is sustained."—Aikin's *Dictionary*—Art. IRON.

An extremely important part of the chemical history of iron relates to the varieties of the metal which are found in commerce. These are much too numerous to be dwelt upon here; so that we shall limit our observations to the principal of them only, which are *cast iron*, *wrought iron*, and *steel*.

Of cast iron there are two principal varieties, distinguished by the terms *white* and *gray*. The first is very hard and brittle, and, when broken, of a radiated texture. Acids act upon it but slowly, and exhibit a texture composed of a congeries of plates, aggregated in various positions.—Daniell, *Quarterly Journal of Science and Arts*, vol. ii. p. 280.

Gray or mottled iron is softer and less brittle; it may be bored, and turned in the lathe. When immersed in dilute muriatic acid, it affords a large quantity of black insoluble matter, which Mr. Daniell considers as a triple compound of carbon, iron, and silicium, and which has some very singular

properties. The texture of the metal resembles bundles of minute needles.

Cast iron, after it has been, to a certain extent, *refined*, by refusion in a forge, in contact with charcoal, is in this country converted into wrought iron by a curious process, called *puddling*. The cast iron is put into a reverberatory furnace, and when in fusion is stirred, so that every part may be exposed to the air and flame. After a time the mass heaves, emits a blue flame, and gradually grows tough, and becomes less fusible, and at length pulverulent; the fire is then urged, so that the particles again agglutinate at a welding heat, and are gradually wrought up into masses. In that state of intense heat the masses are passed successively between rollers, by which a large quantity of extraneous matter is squeezed out, and the bars are now malleable. They are cut into pieces, placed in parcels in a very hot reverberatory, and again hammered or rolled out into bars. They are thus rendered more tough, flexible, and malleable, but much less fusible, and may be considered as nearly pure iron.

Analysis shows that cast iron contains oxygen, carbon, often sulphur and phosphorus, either silica or silicium, and it appears very probable that calcium exists in some of the varieties. A specimen of cast iron analyzed by Berzelius afforded iron 91.53—manganese 4.57—carbon 3.90.

By the processes of puddling and rolling, the principal part of the foreign substances are burned away or squeezed out, and thus malleability is conferred upon the metal by rendering it more pure.

A bar of wrought iron, when its texture is examined in the mode pointed out by Mr. Daniell, presents a fasciculated appearance, the fibres running in a parallel and unbroken course throughout its length. This structure may be well seen by tearing a bar of wrought iron asunder.

Steel is a compound of iron with carbon, the proportions being variable. It combines the fusibility of cast with the malleability of bar iron, and when heated and suddenly cooled it becomes very hard, whence its superiority for the manufacture of cutting instruments. If kept for a long time in fusion it loses carbon and becomes pure iron.

Iron is converted into steel by a process called *cementation*, which consists in heating bars of the purest iron in contact with charcoal: it absorbs carbon and increases in weight, at the same time acquiring a *blistered* surface. This, when drawn down into smaller bars and beaten, forms *titled steel*; and this broken up, heated, welded, and again drawn out into bars, forms *shear steel*. *English cast steel* is prepared by fusing blistered steel with a flux composed of carbonaceous and vitrifiable ingredients, casting it into ingots, and afterwards, by gentle heating and careful hammering, giving it the form of bars.

Messrs. Stodart and Faraday found, that by intensely heating pure steel with charcoal powder, a *carburet of iron* of a dark grey colour, very brittle and highly crystalline, was formed, which afforded, upon analysis,

94.36 iron
5.64 carbon
100

In this compound, which was frequently made and afforded the same results on analysis, and which therefore may be regarded as definite, the proportion of carbon very far exceeds that in steel, so that the latter is probably a compound of pure iron with a variable proportion of the true carburet.

The following table, drawn up by Mr. Mushet, shows the quantities of charcoal which disappeared during the conversion of iron into the different *subcarburets of iron* known in commerce.—*Phil. Mag.* xiii. :—

Charcoal absorbed.	RESULTS.
$1\frac{1}{2}\bar{9}$	soft cast steel
$1\frac{1}{9}\bar{6}$	common cast steel
$\frac{1}{5}\bar{6}$	the same, but harder
$\frac{1}{5}\bar{6}$..	the same: too hard for drawing
$\frac{1}{2}\bar{5}$	white cast-iron
$\frac{1}{2}\bar{6}$	mottled cast-iron
$\frac{1}{5}\bar{9}$	black cast-iron

When the carbon amounts to $\frac{1}{5}\bar{9}$ of the whole mass, the hardness is at a maximum.

The identity of charcoal and diamond above adverted to, receives additional proof by the conversion of iron into steel when that metal is ignited with diamond powder. Upon this

subject some controversy will be found in the *Philosophical Magazine*, vol. v.; the *experimentum crucis* is, however, due to Mr. Pepys, who availed himself of Mr. Children's Voltaic battery of large plates for the production of the requisite heat: (*Phil. Trans.* 1815, p. 371) he bent a wire of pure soft iron so as to form an angle in the middle, in which part he divided it longitudinally by a fine saw; in the opening so formed he placed diamond powder, securing it in its situation by two finer wires, laid above and below it, and kept from shifting by another small wire, bound firmly and closely round them. All the wires were of pure soft iron, and the part containing the diamond powder was enveloped by thin leaves of talc. Thus arranged, the apparatus was placed in the electrical circuit, where it was kept red hot for six minutes; on opening the wire the diamond had disappeared, the interior surface of the iron had fused into numerous cavities, notwithstanding the very moderate heat to which it had been exposed, and all that part which had been in contact with the diamond was converted into perfect blistered steel. A portion of it being heated red and plunged into water, became so hard as to resist the file and to scratch glass.

Wootz or *Indian steel* is truly valuable for the purpose of making edge tools. Its peculiar excellence is owing to combination with a minute portion of the earths alumina and silica; or rather, perhaps, with the bases of these earths. (*Quarterly Journal of Science*, vii., 288.) Whether the earths are found in the ore, or are furnished by the crucible used in making the steel, is not certainly known; nor is the Indian steel-maker probably aware of their presence. *Wootz*, in the state in which it is imported, is not fit to make into fine cutlery. It requires a second fusion, by which the whole mass is purified and equalized, and fitted for forming the finest edge instruments.

The texture of steel, as exhibited by the action of an acid, is not fibrous, but appears somewhat lamellated.

When steel is heated to a cherry-red colour, and then plunged into cold water, it becomes so extremely hard and brittle, as to be unfit for almost any practical purpose. To reduce it from its extreme hardness is called by the workmen *tempering*, and is effected by again heating the steel to a certain

point. The surface being a little brightened, exhibits, when heated, various colours, which constantly change as the temperature is increased, and by these colours it has been customary to judge of the temper of the steel.

A more accurate as well as convenient method is to use a bath and thermometer; the bath may be of mercury, or of the fusible mixture of lead, tin, and bismuth, or, indeed, of any fluid whose boiling point is not much under 600° . Into this bath the articles to be tempered are put, together with the bulb of a thermometer graduated to near the boiling point of mercury. The corresponding degrees of which the various colours appear are from 430° to 600° . The first change is at about 430° , but this is too faint to be distinguished, except by comparison with another piece of untempered polished steel. At 460° the colour is straw, becoming deeper as the temperature is increased; at 500° the colour is brown; this is followed by a red tinge with streaks of purple, then purple, and at nearly 600° it is blue.

The degrees at which the respective colours are produced being thus known, it follows that the workman has only to heat the bath, with its contents, up to the required point. For example, suppose the blade of a penknife (or one hundred of them) to require tempering: they are suffered to remain in the bath until the mercury in the thermometer rises to 460° , and no longer, that being the heat at which the knife (supposing it to be made of the best English cast steel) will be sufficiently tempered.

The advantages attending this method are obvious: the heat is equally applied to the whole; and the workman, instead of attending to the colour of each blade, has only to observe the thermometer.

Some recent experiments, proving that steel, for certain uses, is sufficiently tempered long before it is heated to produce any change of colour, promise to give additional value to this process by a thermometer. The knife edges attached to the pendulum described by Capt. Kater, *Phil. Trans.* 1818, p. 38. were forged by Mr. Stodart, from a piece of fine wootz. They were carefully hardened, and tempered in the bath at 430° ; on trial they were found too soft. They were a second time hardened, and then heated to 212° . The intention was

to increase the heat from that point, trying the temper at the advance of about every ten degrees. In the present instance this was not necessary, the heat of boiling water proving to be the exact point, at which the knife edges were admirably tempered.

It is highly probable that steel, for many uses, may be sufficiently tempered in a range so extensive as from 212° to 430° , and, by the thermometer, all the intervening degrees may certainly be ascertained.

That the colour produced on the surface of heated steel is the effect of oxidation, is proved from the circumstance that when steel is heated and suffered to cool under mercury or oil, none of the colours appear; nor do they when it is heated in hydrogen or nitrogen.

Steel is improved by combination with some other of the metals, forming valuable alloys. (See SILVER.) They seem to require some difference in treatment from the workman, particularly in tempering.—*Quarterly Journal of Science*, vol. ix., p. 319.

Section X. ZINC.

ZINC is found in the state of oxide and of sulphuret. It may be obtained pure by dissolving the purest kinds of zinc that occur in commerce in dilute sulphuric acid, and immersing a plate of zinc for some hours in the solution, which is then filtered, decomposed by carbonate of potassa, and the precipitate ignited with charcoal in an iron or earthen retort. The zinc being volatile at a white heat may thus be distilled over into water, care being taken that the neck of the retort is short and wide, otherwise it will be stopped up by the condensed metal.

The common zinc of commerce generally contains a portion of lead, copper, iron, traces of arsenic and manganese, and a little plumbago: these impurities chiefly remain in the form of a black powder when it is dissolved in dilute sulphuric acid.

Zinc is a bluish white metal, of a specific gravity of about

6.8 in its usual state; but, when drawn into wire, or rolled into plates, its density is augmented to 7 or 7.2. In its ordinary state, at common temperatures, zinc is tough, and with difficulty broken by blows of the hammer. It becomes very brittle when its temperature approaches that of fusion, which is about 680° ; but at a temperature a little above 212° , and between that and 300° , it becomes ductile and malleable, and may be rolled into thin leaves, and drawn into moderately fine wire, which, however, possesses but little tenacity. When a mass of zinc which has been fused is slowly cooled, its fracture exhibits a lamellar and crystalline texture.

Zinc and Oxygen.—When zinc filings are put into water, and air carefully excluded, they suffer no change; but if air be admitted hydrogen is gradually evolved, and the metal becomes encrusted with a gray powder. The same product is obtained by long exposure of zinc to moist air, or by exposing the metal to the joint action of heat and air at a temperature just sufficient to fuse it. This is probably a mere mixture of metallic zinc and oxide of zinc, but by some it has been regarded as a true *suboxide*, and is obtained, according to Dulong, by decomposing oxalate of zinc at a red heat in a retort.

The true salifiable *Oxide of Zinc* is obtained by intensely heating the metal exposed to air. At a high red heat it takes fire, and air being freely admitted, burns with a very bright flame, and is converted into a white flocculent substance, formerly called *nihil album*, *philosopher's wool*, and *flowers of zinc*. As prepared by combustion it contains small particles of the metal, which always render it gritty, and require to be separated by washing; hence, for pharmaceutical use, it is best prepared by precipitating solution of sulphate of zinc by ammonia, and washing and drying the precipitate. It has been used as a pigment, both with oil and water; and is employed in medicine as a tonic, and as an external application. It is sometimes made upon a large scale, and is then seldom pure, being tainted by oxide of iron and other substances: the whiter parts of such oxide used to be called *pompholix*, and the grey, or less pure portions, *tutty*. If it be removed in large flakes from the crucible in which it is forming, and carried into a dark room, they continue for a long time lumi-

nous. This oxide, when pure, is perfectly white; at a high temperature it acquires a tint of yellow, but again whitens as it cools. It is readily soluble in the acids; it also dissolves in the caustic fixed alkalis, and in pure and carbonated ammonia. The strong ammoniacal solution becomes turbid when diluted, and deposits its oxide when boiled. The solutions in potassa and soda yield a white deliquescent mass on evaporation: these, however, can scarcely be called chemical combinations. When a solution of alumina in caustic potassa is mixed with an ammoniacal solution of oxide of zinc, a definite combination of the earth and oxide is thrown down, containing, according to Berzelius, 6 proportionals of alumina and 1 of oxide of zinc, and being identical in composition with the mineral called *Galnite*. The solutions of zinc precipitated by the alkalis furnish bulky white precipitates, consisting of *hydrated oxide*, and which loses water at a red heat, and is then of the same composition as the oxide obtained by the rapid combustion of the metal; it consists of

1 proportional of zinc	= 34
1 ,, oxygen	= 8
Equivalent of oxide of zinc	= 42

Thenard has described a *peroxide of zinc* obtained by agitating the hydrated oxide with oxygenated water: at all events this is no permanent compound, and certainly forms no distinct salts with the acids; we may, therefore, reject the suboxide and the peroxide of zinc as definite compounds, and consider this metal as susceptible of one degree of oxydizement only.

Chloride of Zinc is formed by heating leaf zinc in chlorine, or by evaporating a solution of zinc in muriatic acid to dryness, and heating the residue red-hot in a glass tube. It is also obtained by distilling a mixture of zinc filings and corrosive sublimate, or a mixture of dried sulphate of zinc and chloride of sodium. It is a grey semitransparent substance, fusible at about 212° , and was formerly called *butter of zinc*. It is readily soluble in water, and the solution gives on evaporation a difficultly crystallizable and deliquescent salt, generally called *muriate of zinc*, and which, when heated in the open air, partly sublimes in the form of chloride, and is partly resolved into muriatic acid and oxide of zinc in consequence of the presence of water.

Its concentrated solution deposits oxide of zinc upon the addition of water, and the diluted solution dissolves the oxide when concentrated by evaporation. The solution of muriate of zinc is always slightly acid, and the addition of ammonia does not render it neutral till all the oxide is precipitated. Chloride of zinc consists of

1 proportional of zinc	= 34
1 ,, chlorine	= 36
	<hr/>
Equivalent of chloride of zinc	= 70

The attraction of zinc for chlorine is very great, and this metal may, therefore, often be employed for separating chlorine from other combinations.

Chlorate of Zinc crystallizes in octoëdra, and is a very soluble salt. It is best obtained by dissolving carbonate of zinc in chloric acid. When metallic zinc is digested in chloric acid, a portion of chloride of zinc is formed.

Iodine and Zinc readily combine, and produce a fusible, volatile, and crystalline compound, which, when exposed to air, deliquesces into *hydriodate of zinc*. Heated in contact of air, it is resolved into iodine and oxide of zinc. It consists of

1 proportional of zinc	= 34
1 ,, iodine	= 125
	<hr/>
Equivalent of iodide of zinc	= 159

Iodate of Zinc.—When iodate of potassa is added to solution of sulphate of zinc, it forms a very difficultly soluble iodate of zinc.

Bromide of Zinc.—The action of bromine and of bromic acid upon zinc has not been particularly examined.

Fluoride of Zinc is very difficultly soluble: with fluoride of potassium it forms a more soluble triple salt.

Nitrate of Zinc is a deliquescent salt, which crystallizes with difficulty in four-sided prisms. They are copiously soluble in water and alcohol, and consist of one proportional of acid, one of oxide, and six of water.

Sulphuret of Zinc exists native under the name of *Blende*. It may be formed artificially by heating oxide of zinc with sulphur, and is then of a yellow brown colour. It is also pro-

duced by heating rapidly a mixture of zinc filings and sulphuret of mercury : the mercury is revived, and intense action ensues during the union of the zinc and sulphur. By passing the vapour of sulphur over fused zinc, Mr. E. Davy obtained a white crystalline substance resembling native phosphorescent blende. Sulphuret of zinc consists of

1	proportional of zinc	= 34
1	„ sulphur	= 16
	Equivalent of sulphuret of zinc	<u>= 50</u>

Blende is a brittle soft mineral, of different shades of brown and black. Its primitive form is the rhomboidal dodecaëdron. It usually contains traces of iron and lead. It is an abundant mineral, and important as a source of the pure metal, which is obtained by roasting the ore, and afterwards exposing it to heat in proper distillatory vessels, mixed with charcoal. The English miners call it *black jack*.

Hyposulphite of Zinc was formed long ago by Fourcroy, who considered it as a *sulphuretted sulphite*. He formed it by digesting metallic zinc in sulphurous acid, sulphuretted hydrogen is disengaged, and by gentle evaporation crystals are obtained, which are to be digested in alcohol ; this liquid dissolves the hyposulphite, and affords it in prismatic crystals. A mixture of oxide of zinc and sulphur treated by sulphurous acid affords the same salt ; it is efflorescent, and easily decomposed by heat.—FOURCROY, *Système des Connoissances Chimiques*, v. 380.

Sulphite of Zinc is easily formed by dissolving the oxide in sulphurous acid ; it is more easily crystallizable than the hyposulphite, and is insoluble in alcohol.

Hyposulphate of Zinc is obtained by adding a solution of hyposulphate of baryta to sulphate of zinc ; it is very soluble, and difficultly crystallizable.

Sulphate of Zinc.—The metal is readily oxidized and dissolved by dilute sulphuric acid, hydrogen gas holding a little zinc in solution is given off, and a transparent colourless solution of sulphate of zinc results, which, by evaporation, affords crystals in the form of four-sided prisms, terminated by four-sided pyramids. They have been described by Mr. Brooke

(*Ann. of Phil.*, N. S., vi. 437). This salt is soluble in 2.5 parts of water at 60°. It is prepared for the purposes of the arts from the native sulphuret, and is usually in the form of a white amorphous mass, called *white vitriol*, and is extremely impure. Sulphate of zinc consists of

1	proportional of oxide of zinc	.	.	.	=	42
1	„ sulphuric acid	.	.	.	=	40
						<hr/> 82

The crystals include seven proportionals of water, and consist, therefore, of

Anhydrous sulphate of zinc	=	82
Water (9 × 7)	=	63
						<hr/> 145

Ammonio-sulphate of Zinc is obtained, according to Thomson, by mixing solutions of the two constituent salts in the atomic proportions and concentrating the solution. It crystallizes in white rhomboids, which readily dissolve in water, and consist of

1	proportional of sulphate of zinc	.	.	.	=	82
1	„ sulphate of ammonia	.	.	.	=	57
7	proportionals of water (9 × 7)	.	.	.	=	63
						<hr/> 202

Sulphate of Zinc and Potassa forms flat rhomboidal crystals, permanent in the air, and consisting of

1	proportional of sulphate of zinc	.	.	.	=	82
1	„ sulphate of potassa	.	.	.	=	88
7	proportionals of water (9 × 7)	.	.	.	=	63
						<hr/> 233

Native Sulphate of Zinc is found at Holywell in Flintshire, and in other places where the sulphuret of zinc occurs; it is probably the result of the decomposition of that ore.

Sulphuret of Zinc is a brilliant lead-coloured compound, formed by distilling in a coated retort a mixture of two parts of zinc, and one of phosphorus.

Neither *Hypophosphite* nor *Phosphite of Zinc* have been examined.

Phosphate of Zinc is not crystallizable. It may be obtained by dissolving zinc in phosphoric acid, and evaporating to dry-

ness. A phosphate of zinc is also precipitated upon the addition of phosphate of soda to sulphate of zinc. These salts have not been precisely examined, but it is probable there is a phosphate and a biphosphate of zinc.

Carbonate of Zinc occurs native, forming one of the varieties of the mineral called *calamine*. It may be formed by passing carbonic acid through water containing diffused hydrated oxide of zinc. The precipitate formed by adding carbonate of potassa to sulphate of zinc, is, according to Berzelius, a mixture of carbonate and hydrated oxide. The carbonate of zinc consists of

1	proportional of oxide of zinc	.	.	.	= 42
1	„ carbonic acid	.	.	.	= 22
					<hr/> 64

The primitive form of calamine, which occurs both crystallized and massive, is an obtuse rhomboid. It is often found investing carbonate of lime, which has sometimes been decomposed, and the calamine remains in pseudo-crystals. This mineral abounds in Somersetshire, Flintshire, and Derbyshire. A beautiful variety, coloured by carbonate of copper, is found at Matlock. A variety of calamine, known by the name of *electric calamine*, from its property of becoming electrical when gently heated, consists of oxide of zinc in combination with silica.

The zinc of commerce is procured from the native sulphuret and from calamine by the following process. The ore is first picked and broken into small pieces, and then submitted to a dull red heat in a reverberatory furnace, by which carbonic acid is driven off from the calamine, and sulphur from the blende. It is then washed, ground, and thoroughly mixed with about one-eighth its weight of powdered charcoal. This mixture is put into large earthen pots, not unlike oil jars, six of which are usually placed in a circular furnace; each pot has an iron tube passing from its lower part, through the floor of the furnace, and dipping into water; they are everywhere else firmly luted: upon the application of a red heat, the metal distils through the tube into the water beneath, whence it is collected, melted, and cast into cakes.

Borate of Zinc is an insoluble white powder.

Ferrocyanate of Potassa produces a yellowish-white precipitate in solutions of zinc.

The salts of zinc are mostly soluble in water, and the solutions are colourless and transparent, and have a peculiarly unpleasant metallic taste: they are not precipitated by hydriodic acid. Potassa, soda, and ammonia, form white precipitates, soluble in excess of the alkali, and of sulphuric acid. Hydro-sulphuret of ammonia produces a yellowish-white precipitate. The soluble phosphates, carbonates, and borates, produce white precipitates. Infusion of galls occasions no precipitates.

Alloys of Zinc.—With potassium and sodium, zinc forms brittle alloys, decomposable by exposure to air and water. Its alloy with manganese is unknown. With iron it forms a white and somewhat malleable alloy, which is difficult to form; but if plates of hot iron be dipped into melted zinc, they acquire the appearance of tin plate. Brass is an alloy of copper and zinc, afterwards to be described.

Section XI. TIN.

THIS metal has been known from the remotest ages. It was in common use in the time of Moses, and was obtained at a very early period from Spain and Britain by the Phœnicians. —PLINY, lib. iv. cap. 34, and xxxiv. cap. 47. Several varieties of tin occur in commerce, respecting which Vauquelin has given an useful essay in the 77th volume of the *Annales de Chimie*.

The native oxide is the principal ore of tin: the metal is obtained by heating it to redness with charcoal and a little lime. The common ores are known under the name of *mine-tin*, and furnish a less pure metal than that obtained from *stream-tin*. The former is usually called *block-tin*, the latter *grain-tin*. The processes of reduction are described at length in Aikin's *Dictionary* (Art. TIN); and by Mr. Taylor, in the 5th volume of the *Geological Transactions*.

Tin has a silvery white colour; it is malleable, though sparingly ductile. Sp. gr. 7.30. It melts at 440° , and, by exposure to heat and air, is gradually converted into a white peroxide. Placed upon ignited charcoal, under a current of oxygen gas, it enters into rapid combustion; and if an intensely heated globule of the metal be thrown upon a sheet of paper, it subdivides into small particles, which burn very brilliantly.

A preparation under the name of *powdered tin* is sometimes directed to be prepared for pharmaceutical use, by shaking the melted metal in a wooden box rubbed with chalk on the inside: *tin filings* have also a place in some *Pharmacopœia*, and have been used as a vermifuge. These preparations are, however, both dangerous, the metal being rendered poisonous in the former case by slight oxidation (Orfila, *Traité des Poisons*, tom. i. 2me partie, p. 18), and often creating very dangerous irritation when given in filings.

Protoxide of Tin is obtained by precipitating protomuriate of tin by ammonia; it falls in the state of hydrate; when dried, out of the contact of air, it is of a gray colour, and undecomposable by heat. According to M. Cassola (*Ann. of Phil.* xiii. 40) the protoxide is also obtained by pouring nitric acid diluted with ten times its volume of water upon tin filings, and leaving them in contact 48 hours. When protomuriate of tin is precipitated by a carbonated alkali, and the precipitate carefully dried at a temperature below 212° , it is a hydrated protoxide, retaining no trace of carbonic acid. It dissolves when in the state of hydrate in the alkalis; exposed to heat and air, it passes into the state of peroxide, undergoing a faint combustion. Its ammoniacal solution, when long kept, deposits metallic tin in arborescent crystals, and becomes a solution of the peroxide. The solution in the fixed alkalis undergoes the same change.

Peroxide of Tin is formed by treating the metal with nitric acid: there is a violent action attended by the formation of nitrate of ammonia. Scarcely any of the metal is dissolved, but remains as a yellowish powder, which may be purified by washing. It is also formed by heating tin filings with red oxide of mercury; and by projecting a sufficient quantity of nitre upon red-hot tin. This oxide when in the state of hydrate dissolves in the alkalis and their carbonates. Fused

with glass, it forms *White Enamel*. Heated intensely it loses a portion of oxygen, and undergoes fusion. It does not readily dissolve in acids, except it be in the state of hydrate, and then muriatic acid dissolves it.

The substance called *Tin Putty*, is an oxide of tin formed by levigating the crusts of oxide that form upon the metal when kept for some time in fusion.

Native Peroxide of Tin is found in Cornwall; in Spain; and in Saxony: it has also been found in Brittany, in France; in the East Indies; and in South America. The specific gravity of the native oxide is 7: its primitive crystal is an obtuse octoëdron, of which the modifications are extremely numerous. (W. PHILLIPS, *Geological Transactions*, vol. ii.) In some of the valleys of Cornwall, tin is found in rounded nodules, of various sizes, mixed with pebbles and rounded fragments of rocks. To separate the tin from the alluvial matter, currents of water are passed over it, and hence these deposits have been called *stream works*, and the tin ore, *stream tin*. One of the most extensive of these is a branch of Falmouth Harbour.

A modification of stream tin is called *wood tin*. It usually appears in small banded fragments of globular masses.

The protoxide of tin consists of

1 proportional of tin	=	58
1	„	oxygen	= 8
							<hr/>
Equivalent of protoxide of tin	=	66

The peroxide is a compound of

1 proportional of tin	=	58
2 proportionals of oxygen	(8 × 2)	=	16
							<hr/>
							74

Both these oxides of tin form salts, but the protoxide is the true salifiable base: the salts of the peroxide are less defined and permanent, and in its property of uniting to the alkalis, it manifests properties which approach to those of an acid.

Tin and Chlorine.—*Protochloride of Tin* is procured by heating together an amalgam of tin and calomel; or more simply by heating protomuriate of tin in a retort till it fuses; it is a grey semi-transparent crystalline solid, which dissolves in water, forming the solution usually called *protomuriate of*

tin; it is volatile at a red heat. Heated in chlorine it burns into perchloride of tin. It is composed of

1 proportional of tin	= 58
1 „ chlorine	= 36
					<hr/>
Equivalent of protochloride of tin	= 94

If tin be heated in excess of chlorine, or if amalgam of tin be distilled with corrosive sublimate, a *perchloride* is obtained. The best proportions are six parts of tin, previously combined with one of mercury, and intimately mixed with thirty of corrosive sublimate. The mixture is put into a glass retort with a sufficiently capacious receiver luted to it, and may be distilled over a small charcoal fire. The heat should be slowly raised, to prevent too sudden action. Towards the end of the process a little chloride rises, which the old chemists, from its consistency and appearance, called *Butter of Tin*. It may also be procured by distilling 8 ounces of finely-powdered tin with 24 of corrosive sublimate. It is a transparent colourless fluid, and when poured into water, is instantly converted into *permuriate of tin*; mixed with one-third its weight of water it concretes into a saline mass. It was formerly called *Libavius's Fuming Liquor*: it exhales copious fumes when exposed to a moist air, and produces muriatic acid and oxide of tin. It is instantly decomposed by metallic zinc, forming chloride of zinc and a precipitate of metallic tin. It consists of

1 proportional of tin	= 58
2 proportionals of chlorine (36 × 2)	= 72
					<hr/>
Equivalent of perchloride of tin	= 130

Chlorate of Tin has not been examined.

The *Protomuriate of Tin*, used by dyers, may be obtained by boiling one part of tin with two of muriatic acid; a small portion of insoluble black powder generally remains, together with some undissolved tin. This solution, which is always acid, quickly absorbs oxygen from the air and from several compounds, and if added to certain metallic solutions, revives or deoxidizes them. With solution of gold it produces a purple precipitate used in painting porcelain, and known under the name of *Purple of Cassius*. It decomposes and precipitates sulphur from sulphurous acid. It crystallizes from its

concentrated solution in deliquescent crystals. With infusion of cochineal it produces a purple precipitate, and it is a compound much used to fix and change colours in the art of dyeing and calico printing. This muriate of tin is the *Sal Jovis* of old writers, Jupiter being the name by which the alchemists distinguished this metal*.

When potassa is added to muriate of tin, a *submuriate* of the protoxide is thrown down, containing, according to J. Davy, 70.4 protoxide, 19 muriatic acid, 10.6 water. These numbers coincide with 2 proportionals of oxide + 1 of acid.

The *Permuriate of Tin* (muriate containing the peroxide) may be formed by dissolving the metal in nitro-muriatic acid, or by exposing the muriate to air. It forms acicular crystals in the upper parts of phials containing the bi-chloride imperfectly secured from air; and is directly formed by adding water to the bi-chloride, which excites much heat, and forms a concrete mass easily fusible and soluble in water. It does not occasion precipitates in the metallic solutions, and produces a scarlet colour with infusion of cochineal.

The dyers prepare this solution of tin by digesting the filings of the metal in single aquafortis (nitric acid, sp. gr. 1.3) to each pound, of which they add about two ounces of common salt or of sal-ammoniac. This compound acid takes up about one-eighth its weight of tin.

The pure fixed alkalis added to this salt of tin, occasion a precipitate, which has not been accurately examined, but is said to be a *subpermuriate*. The hydrated peroxide of tin is more readily soluble in alkalis than the protoxide; it has been by some termed *Stannic Acid*.

Several triple salts, with a base of muriate of tin, have been described, but they are of little importance.

Iodide of Tin may be formed directly by heating the metal with iodine; or indirectly, by adding hydriodic acid to a solution of muriate of tin. It is an orange-coloured compound, and has not been analyzed.

Iodate of Tin has not been examined.

Bromide of Tin. Tin and bromine act energetically: the

* On the preparation of Muriate of Tin, see Berard (*Ann. de Chim.* lxxviii, 78) and Chaudet (*Ann. de Chim. et Phys.* iii. 376).

metal burns, and a white crystallized compound is obtained, readily fusible and volatile, yielding slight vapours in moist air, and dissolving in water. *Bromate of Tin* has not been examined.

Fluoride of Tin is a soluble and crystallizable compound.

Nitrate of Tin may be formed by acting upon the metal by dilute nitric acid; a yellow solution, which will not crystallize, is obtained; exposed to air it absorbs oxygen, and peroxide of tin precipitates. If evaporated, the peroxide falls, and a portion of nitrate of ammonia is formed. It is evident, therefore, that part of the water, as well as of the acid, are here decomposed.

Tin and Sulphur.—There are two sulphurets of tin. That containing 1 proportional of metal + 1 of sulphur, may be procured by heating tin with sulphur; it is of a deep bluish colour, and crystallizes in long needles. In consequence, however, of the high temperature required for its formation, so much of the sulphur is generally lost, that a mixture of the metal and of the sulphuret is only obtained. This mixture may be pulverized and heated in a retort with its weight of sulphur, in which case the sulphuret is the result. A sulphuret of tin is also precipitated, when the salts of the protoxide are mixed with solution of sulphuretted hydrogen. Its components are

1 proportional of tin	.	.	.	= 58
1 „ sulphur	.	.	.	= 16
Equivalent of sulphuret of tin	.	.	.	<hr/> = 74

Bisulphuret of Tin is of a bright golden yellow colour, and flaky structure, and has been termed *Aurum Musivum*. It is formed by heating peroxide of tin with its weight of sulphur. Mr. Woulfe has given a formula for its production (*Phil. Trans.* 1771); but the following, taken from the *London New Dispensatory* of 1765, answers best. Take 12 oz. of tin and amalgamate it with 6 oz. of mercury, reduce it to powder, and mix it with 7 oz. of flowers of sulphur and 6 oz. of sal ammoniac, and put the whole into a glass matrass placed in a sand heat. Apply a gentle heat till the white fumes abate, then raise the heat to redness, and keep it so for a due time. On cooling and breaking the matrass, the *Mosaic gold* is found at

the bottom.—See Woulfe's *Paper*, and Aikin's *Dict.*—art. **TIN**. This compound is also formed by decomposing perchloride of tin by sulphuretted hydrogen. Bisulphuret of tin is insoluble in the acids, except in nitro-muriatic acid: it is soluble in caustic potassa, but not without partial decomposition.

Hyposulphite of Tin has not been examined. Protomuriate of tin forms no precipitate with the alkaline hypsulphites.

Sulphite of Tin is formed by digesting the protoxide in sulphurous acid, but the salt has not been examined.

Sulphates of Tin.—When tin is boiled in sulphuric acid, a solution is obtained which deposits white acicular crystals of *protosulphate of tin*. It is also precipitated by pouring sulphuric acid into protomuriate of tin. The hydrated peroxide of tin is also soluble in sulphuric acid.

Phosphuret of Tin may be formed by dropping phosphorus into melted tin. It is of a silvery colour, sectile, and somewhat ductile. When its filings are sprinkled upon hot coals the phosphorus burns.

Phosphite of Tin has not been examined.

Phosphate of Protoxide of Tin is formed by adding phosphate of soda to the protomuriate. It is a white powder, not soluble in water, and fuses at a red heat into an opaque white enamel.

Carbonate of Tin.—When carbonate of potassa is added to protomuriate of tin, a white precipitate ensues, which, when washed and dried, loses carbonic acid.

Borate of Tin is an insoluble white powder.

Ferrocyanate of Potassa produces a white precipitate in solution of muriate of tin.

The salts of tin are mostly soluble in water. They are precipitated, of an orange colour, by hydriodic acid, and by hydrosulphuret of ammonia, provided no excess of acid be present. Solution of muriate of gold, and of corrosive sublimate, produce purple and black precipitates in the salts of tin containing the protoxide, but none in those containing the peroxide.

Alloys of Tin.—With potassium and sodium tin forms brittle white alloys. Its alloy with manganese is not known. It does not readily combine with iron, but tin-plate may be

considered as an imperfect alloy of those metals. With zinc it forms a hard brittle alloy. (On the alloys of tin, see Dus-saussy, *Ann. de Chim. et Phys.* v., and Chaudet, in same work, v. and vii.)

Section XII. CADMIUM.

THIS metal is contained in certain ores of zinc, and especially in the black fibrous Blende of Bohemia. It has been detected by Dr. Clarke in the calamine of Derbyshire and Somersetshire, and in the zinc of commerce; (*Annals of Phil.* xv. 272; and New Series, iii. 123;) and Mr. Herapath found it in considerable proportion in the sublimate which, in the process for obtaining zinc, rises before that metal, forming what the workmen call the *brown blaze*. (*Ann. of Philos.* iii. 435.) It may be procured by digesting the ore in muriatic acid, by which a mixed muriate of zinc and cadmium is obtained: it should be evaporated to dryness, to drive off excess of acid, and re-dissolved in water. Immerse a plate of iron into this solution, to separate all that may be thus precipitated, and afterwards filter the liquor into a platinum capsule containing a piece of zinc. The cadmium will coat over the surface of the capsule, and adhere so firmly to it, that it may be washed, and thus freed from any remaining solution of zinc. Muriatic acid dissolves the precipitate with effervescence, and from this solution it is thrown down white by the alkalis, and yellow by sulphuretted hydrogen. (Wollaston.)

M. Stromeyer separates cadmium from the ores containing it, by digesting them in dilute sulphuric acid, and passing sulphuretted hydrogen through the acidulous solution. He washes the precipitate thus formed, dissolves it in muriatic acid, and expels the excess of acid by evaporation. He then redissolves the residue in water, precipitates by carbonate of ammonia, of which an excess is added, for the purpose of retaining the oxides of zinc and copper in solution; the remaining carbonate of cadmium is washed, dried, and heated with lampblack, by which it is easily reduced.

The physical properties of cadmium closely resemble those of tin: its specific gravity is 8.63, and somewhat exceeds 9. after hammering. It fuses and volatilizes at a temperature a little below that required by tin, and its vapour is inodorous. Air does not act upon it except when heated, when it forms an orange-coloured oxide, not volatile, and easily reducible.

Oxide of Cadmium readily dissolves in acids; it is precipitated by potassa in the state of a white hydrated oxide, soluble in ammonia, but insoluble in potassa and soda, and capable of absorbing carbonic acid. The alkaline carbonates throw down a white anhydrous carbonate of cadmium, insoluble in excess of carbonate of ammonia. Phosphate of soda forms a white pulverulent precipitate. Ferropurssiate of potassa and oxalate of ammonia give white precipitates, and infusion of galls produces no change. Sulphuretted hydrogen forms a yellow precipitate in the solution of cadmium, and zinc throws down metallic cadmium.

When the hydrated oxide is heated to redness it becomes brown, and is neither volatile nor fusible; but when mixed with carbonaceous matter it appears volatile, in consequence of its easy reduction, and the burning off of the separated cadmium.

From the experiments of Stromeyer, the number 56 appears to be the equivalent of cadmium, and the oxide consists of

1	proportional of cadmium	.	.	.	= 56
1	„ oxygen	.	.	.	= 8
					—
	Equivalent of oxide of cadmium	.	.	.	= 64

Chloride of Cadmium is obtained by dissolving the hydrated oxide in muriatic acid: on evaporation, small prismatic crystals are obtained, very soluble in water, and efflorescent in a dry atmosphere. These crystals readily fuse into a crystalline mass, which is chloride of cadmium: at a very high temperature it is volatile, and concretes in the form of a lamellar sublimate. It consists of

1	proportional of cadmium	.	.	.	= 56
1	„ chlorine	.	.	.	= 36
					—
	Equivalent of chloride of cadmium	.	.	.	= 92

Iodide of Cadmium is a colourless crystallizable compound,

fusible, and resolved at a high temperature into iodine and cadmium.

Fluoride of Cadmium is a difficultly soluble compound.

Nitrate of Cadmium forms radiated acicular crystals, which are deliquescent, and contain 22 per cent. of water. The dry nitrate consists of

1	proportional of oxide of cadmium	.	.	.	=	64
1	„ nitric acid	.	.	.	=	54
						<hr/>
						= 118

Sulphuret of Cadmium is obtained in the form of a bright yellow powder, by precipitating the solutions of the metal with sulphuretted hydrogen. It is also formed by heating cadmium, or its oxide, with sulphur, and concretes, on cooling, into a yellow lamellar mass. It dissolves with the evolution of sulphuretted hydrogen in concentrated muriatic acid. It consists of

1	proportional of cadmium	=	56
1	„ sulphur	=	16
<hr/>							
Equivalent of sulphuret of cadmium						.	= 72

Sulphate of Cadmium forms transparent prismatic crystals, much resembling those of sulphate of zinc: they are efflorescent, and very soluble in water: gently heated, they lose water of crystallization, and at a higher temperature a part of the acid escapes. They consist of

1	proportional of oxide of cadmium	.	.	.	=	64	} = 104
1	„ sulphuric acid	.	.	.	=	40	
<hr/>							
4	„ water (9 × 4)	.	.	.	=	36	
							<hr/>
							140

Phosphuret of Cadmium is a gray, brittle compound, with a feeble metallic lustre.

The *Phosphate*, *Carbonate*, and *Borate of Cadmium*, are insoluble white powders, consisting of one proportional of oxide and one of the respective acids.

The other compounds of cadmium have scarcely been examined.

Section XIII. COPPER.

THIS metal is found native, and in various states of combination. Of its ores, the oxide, chloride, sulphuret, sulphate, phosphate, carbonate, and arseniate, are the most remarkable. The metal may be obtained perfectly pure by dissolving the copper of commerce in nitric acid; the solution is diluted, and a plate of iron is immersed, upon which the copper is precipitated. It may be fused into a button, after having been previously washed in dilute sulphuric acid to separate a little iron that adheres to it.

It was known in the early ages of the world, and was the principal ingredient in domestic utensils, and in the instruments of war, previous to the discovery of malleable iron. The word *copper* is derived from the island of Cyprus, where it was first wrought by the Greeks.

Copper has a red colour and much brilliancy: it is very malleable and ductile, and has a peculiar smell when warmed or rubbed. It melts at a cherry red or dull white heat. Its specific gravity is 8.89. Under a flame, urged by oxygen gas, it takes fire, and burns with a beautiful green light. Exposed for a long time to damp air, copper becomes covered with a thin greenish crust of carbonate. If heated and plunged into water, a quantity of reddish scales separate, consisting of an imperfect oxide. The same scales fly off during cooling from a plate of the metal which has been heated red hot. Copper does not decompose water at a red heat.

Native Copper occurs in a variety of forms; massive, dendritic, granular, and crystallized in cubes, octoëdra, &c. It is found in Cornwall, Siberia, Saxony, Hanover, Sweden, and America; chiefly, but not exclusively, in primitive rocks.

Copper and Oxygen.—There are two oxides of copper. The red or *protoxide* occurs native. It may be formed artificially, by heating 5 parts of peroxide with 4 of very finely divided metallic copper, or by digesting a mixture of 50 parts of finely divided metallic copper, and 58 of peroxide of copper, in 400 of muriatic acid. When potassa is added to this solution, a *hydrated protoxide*, of an orange colour, falls; if

quickly dried out of the contact of air, it becomes of a red brown. It consists of

1	proportional of copper	= 64
1	„ oxygen	= 8
Equivalent of protoxide of copper							<hr/> = 72

When this oxide is intensely heated, it frequently happens that small octoëdral and cubic crystals are formed in it; the same thing was observed by Mr. Chenevix, on exposing peroxide or hydrate of copper to a violent heat, in an open crucible, without addition; a semifused mass, resembling native red copper, was obtained. (*Phil. Trans.* 1801.)

The dilute acids resolve this oxide into metallic copper and peroxide; but it dissolves in concentrated muriatic acid, forming a dark brown solution, above adverted to. It dissolves in ammonia, as will presently be more fully explained, but it does not dissolve in solutions of potassa or of soda.

The *Native Protoxide*, or *Ruby Copper*, is of a red or steel-gray colour, soft and brittle, and occurs massive, and crystallized in octoëdra, dodecaëdra, and cubes. There is a beautiful variety in fine capillary crystals; and another, which is compact and earthy, called *Tile Ore*. Cornwall abounds in fine specimens of this ore.

Peroxide of Copper is procured by precipitating nitrate of copper by potassa, washing the precipitate, and exposing it to a red heat. It is black, and consists of

1	proportional of copper	= 64
2	„ oxygen (8×2)	= 16
Equivalent of peroxide of copper							<hr/> = 80

The composition of this oxide is learned by dissolving 100 grains of pure copper in nitric acid, evaporating to dryness, and giving the residue a red heat in a porcelain crucible; it is peroxide of copper, and weighs 125 grains: considering this as a compound of 1 proportional of copper and 2 of oxygen, the number 64 will represent the metal; for $25 : 100 :: 16 : 64$.

100 grains of pure native oxide of copper in octoëdral crystals, dissolved in muriatic acid, furnished a precipitate of 89 grains of metallic copper (duly cleansed) upon a plate of iron, so that, from this experiment, the protoxide consists of 89

copper + 11 oxygen; and $11 : 89 :: 86 : 4.7$; a number not quite agreeing with the former, but sufficient to show that the native oxide is a protoxide.

Before the blowpipe, this oxide fuses when intensely heated by the tip of the flame, upon charcoal; by the interior of the flame it readily affords a globule of metal. It is the basis of all the common salts of copper. When alkalis are dropped into its solutions, they throw it down in the form of a bulky blue *hydrate*, which, however, is not permanent at a boiling heat, but becomes the black anhydrous oxide. The peroxide of copper is not soluble in the liquid fixed alkalis; but when carbonate of potassa or of soda are fused with it, it expels carbonic acid, and combines to form a blue or green compound. Its combination with ammonia will presently be noticed. It communicates a green, and sometimes a blue tint to vitreous compounds; and Sir H. Davy has shown that it is the basis of certain colours used by the ancients, which have been supposed to contain cobalt. (*Phil. Trans.* 1815.)

Copper and Chlorine.—Gaseous chlorine acts upon copper with great energy, and produces two chlorides; the one a comparatively fixed fusible substance, which is the *protochloride*. The other a volatile yellow substance, which is a *perchloride*.

The *Protochloride of Copper* was first described by Boyle in 1666, under the name of *Rosin of Copper*. It may be obtained by exposing copper filings to the action of chlorine not in excess: or by evaporating the protomuriate, and heating the residue in a vessel with a very small orifice; or by heating the perchloride in the same way. It is also the residue of the distillation of a mixture of two parts of corrosive sublimate and one of copper filings. It is insoluble in water, but soluble in muriatic acid, from which potassa throws down a protoxide. When water is added to its muriatic solution, it is thrown down in the form of a white granular precipitate: its colour varies, being generally dark brown; but if fused and slowly cooled, it is yellow, translucent, and crystalline. It consists of

1 proportional of copper	=	61
1 " chlorine	=	36
							<hr/>
Equivalent of protochloride of copper	=	100

When moistened chloride of copper is exposed to air it acquires a greenish white colour, and becomes converted into a *subpermuriate of copper*. The same compound may be formed by adding hydrated peroxide of copper to a solution of the permuriate; or by exposing to the atmosphere slips of copper partially immersed in muriatic acid. This compound consists of

2	proportionals of peroxide of copper	(80 × 2)	=	160
1	„	muriatic acid	=	37
2	„	water (9 × 2)	=	18
				<hr/>
				215

Perchloride of Copper may be formed by dissolving peroxide of copper in muriatic acid, and evaporating to dryness by a heat below 400°. It is soluble in water, producing a permuriate, from which potassa precipitates the peroxide; its colour is yellow, but it becomes white and afterwards green when exposed to heat and moisture. Exposed to a red heat in a tube with a very small orifice, gaseous chlorine is expelled, and it becomes a protochloride. It readily absorbs ammonia, and becomes a blue pulverulent mass. It consists of

1	proportional of copper	=	64
2	„ chlorine (36 × 2)	=	72
							<hr/>
	Equivalent of perchloride of copper	=	136

Muriatic acid acts with difficulty on metallic copper, except it be concentrated and boiling; but it readily dissolves the peroxide, forming a brown or grass-green solution, according to its state of dilution. This is a *permuriate of copper*. By carefully evaporating and cooling its solution, it crystallizes in prismatic parallelipeds which are deliquescent, and very soluble in water and alcohol. If plates of copper be exposed to the joint action of air and the fumes of muriatic acid, they become incrustated with a green powder, which is readily soluble in muriatic acid, and composed as the subpermuriate. This compound is sometimes called *Brunswick green*. Immersed in a solution of common salt, a green crust of the subpermuriate is also gradually formed upon copper, and to this change the chief decay of the sheathing of ships is to be attributed. The laws of electro-chemical action, as illustrated by Sir H. Davy, show that the sea-water only thus acts upon the metal when

in a positive state; he, therefore, suggested its protection by rendering the copper electro-negative, and effected this by attaching to it a mass of iron or of zinc. (*Phil. Trans.*, 1824.) This principle has already been explained (page 89), and the plan is theoretically unexceptionable; but there is a practical obstacle not yet overcome, which consists in the difficulty of exactly adjusting the protecting power, so as to render the copper, as it were, neutral; for no sooner does it become in the least over-negative, than earthy substances precipitate upon it, and, although it certainly is protected from corrosion, these form a favourable surface for the attachment of marine animals and vegetables, which collect in such quantities as to impede the sailing of the vessel. For the preservation of the copper of vessels lying in dock, the system may be useful, and they may be cleaned, and the protectors (attached pieces of iron or of zinc) removed, previous to their being sent to sea.

Native Subpermuriate of Copper is found in Peru and Chili, sometimes in the form of green sand, and sometimes massive and crystallized. The green sand was found in the river Lipas, in the desert of Atacama, separating Peru from Chili; hence mineralogists have termed this variety *Atacamite*. Muriate of copper has also been found upon some of the lavas of Vesuvius. The primitive form of this substance is an octoëdron. It is of a deep green colour, and contains, according to Dr. Davy's analysis,

73	peroxide of copper
16.2	muriatic acid
10.8	water

100

Chlorate of Copper is a blue-green deliquescent salt, difficultly crystallizable, formed by dissolving peroxide of copper in chloric acid. A piece of paper dipped into its solution burns with a remarkable green flame.—VAUQUELIN.

An *Iodide of Copper* is precipitated from solutions of the metal by hydriodic acid. It is brown and insoluble.

When solution of iodate of potassa is added to solutions of copper, an insoluble *iodate of copper* is thrown down.

Bromide of Copper has not been examined.

Fluorides of Copper.—When hydrated protoxide of copper is added to hydrofluoric acid, and evaporated out of the con-

tact of air, a fusible compound of a black colour, while hot, but becoming red as it cools, is obtained, which is a *proto-fluoride of copper*. It forms a dark solution in hydrofluoric acid, and is precipitated white by water, but becomes red when collected upon a filter.

When carbonate of copper is dissolved in hydrofluoric acid, carbonic acid is evolved, and an insoluble compound is at length formed, the properties of which are not very explicitly detailed by Berzelius, who alone has examined this and the preceding compound.

Nitrate of Copper.—Nitric acid, diluted with three parts of water, rapidly peroxidizes copper, evolving nitric oxide, and ultimately forming a bright blue solution, which affords deliquescent prismatic crystals on evaporation, of a fine blue colour, and very caustic. They contain a considerable portion of water, which causes them to liquefy at a temperature below 212° . At a higher temperature they lose water and acid, and according to Proust, become a *subpernitrate*, which is insoluble in water, and entirely decomposed at a red heat. This salt may also be formed by adding finely powdered carbonate of lime to a solution of the pernitrate of copper. It is of a green colour, and consists, according to Berzelius, of

Peroxide of copper	•	•	•	66.0	} = 100
Nitric acid	•	•	•	18.9	
Water	•	•	•	15.1	

The anhydrous pernitrate of copper consists of

1 proportional of peroxide of copper	•	•	= 80
2 proportionals of nitric acid (54×2)	•	•	= 108
			<hr/> 188

According to Thomson, the crystals include as much as 14 proportionals (9×14) of water. There appears to be no protonitrate of copper; for protoxide of copper, digested in very dilute nitric acid, is resolved into peroxide, which dissolves, and into metallic copper. Potassa forms, in the solution of the pernitrate, a bulky blue precipitate of *hydrated peroxide of copper*, which, as already observed, when boiled in potassa or soda, becomes black from the loss of its combined water. When crystals of nitrate of copper are coarsely powdered, sprinkled with a little water, and quickly rolled up

beauty, crystallized and massive, in Cornwall, and in Yorkshire. Its colour is gray; its lustre shining and metallic, and it yields easily to the knife. Its primitive form is a six-sided prism, which passes into the dodecaëdron with triangular faces, and various modifications of it.

A variety of black sulphuret of copper, containing iron and arsenic, has been described by Messrs. W. and R. Phillips. It has been termed by the latter *Tennantite*; its most ordinary form is the rhomboidal dodecaëdron either perfect or variously modified.—*Quarterly Journal of Science and Arts*, vol. vii. p. 95.

When solutions of copper are decomposed by sulphuretted hydrogen, a black hydrosulphuretted oxide of copper falls, which, when dried and heated, evolves water, and becomes the black sulphuret.

Copper Pyrites, or *Yellow Copper Ore*, is the most important and generally occurring ore, from which the largest proportion of the copper of commerce is derived; it occurs in a variety of forms, its primitive crystal being the regular tetraëdron. The Cornish mines are very productive of this ore, and it is the principal product of the Parys mountain mine in Anglesea. A beautiful iridescent variety occurs in the Ecton mine in Staffordshire. The composition of the different varieties of copper pyrites, appears in all cases to be sulphur, copper, and iron. The *variegated copper* Mr. Phillips regards as a compound of

- 1 proportional of sulphuret of iron
- 2 proportionals of sulphuret of copper.

Ann. of Phil. iii. 87.

The *yellow copper ore* is also a triple sulphuret of iron and copper; and, omitting the small portion of lead and arsenic with which it is usually contaminated, it may be considered as a compound of

- 2 proportionals of sulphuret of iron
- 1 proportional of sulphuret of copper.

100 parts will thus give—

Sulphur	34.78
Iron	30.44
Copper	34.78
					<hr/>
					100.

PHILLIPS, *Ann. of Phil.* iii. 301.

The following is an outline of the process by which these ores of copper are reduced, as carried on upon a very large scale near Swansea, where the chief part of the Cornish ores are brought to the state of metal. The ore, having been picked and broken, is heated in a reverberatory furnace, by which arsenic and sulphur are driven off. It is then transferred to a smaller reverberatory, where it is fused, and the slag which separates, being occasionally removed, is cast into oblong masses used as a substitute for bricks. The impure metal collected at the bottom of the furnace is granulated by letting it run into water; it is afterwards remelted and granulated two or three times successively, in order further to separate impurities, which are chiefly sulphur, iron, and arsenic, and ultimately cast into oblong pieces called *pigs*, which are broken up, roasted, and lastly melted with a portion of charcoal in the refining furnace. Malleability is here conferred upon the copper, and its texture improved by stirring the metal with a pole of green wood, generally birch, which causes great ebullition and agitation; assays are occasionally taken out, and the metal, originally crystalline and granular when cold, now becomes fine and close, so as to assume a silky polish when the assays are half cut through and broken. The metal is now cast into cakes about 12 inches wide by 18 in length. The whole process of refining the copper, and toughening it by poling, requires much care and attention; and if it be over-poled, the metal is even rendered more brittle than in its original state: the effect of poling has not been satisfactorily explained; it may consist in the separation of a small portion of oxide of copper, and the effect of over-poling may possibly depend upon the combination of the copper with a portion of carbon. Copper for brass making is granulated by pouring the metal through a perforated ladle into water; when this is warm, the copper assumes a rounded form, and is called *bean-shot*; but if a constant supply of cold water is kept up it becomes ragged, and is called *feathered-shot*. Another form into which copper is cast, chiefly for exports to the East Indies, is in pieces of the length of six inches, and weighing about eight ounces each: the copper is dropped from the moulds immediately on its becoming solid into a cistern of cold water, and thus, by a slight oxidation of the metal, the sticks

acquire a rich red colour on the surface. This is called *Japan Copper*. A large quantity of copper is rolled into sheets and sheathings, both for export and home consumption. (For an excellent account of the reduction of copper, as carried on in this country, the reader is referred to Mr. Vivian's paper, *Ann. of Phil. N. S.* v. 113.)

Hyposulphite of Copper was formed by Mr. Herschel by mixing hyposulphite of potassa with sulphate of copper. It is colourless; of an intensely sweet taste; and provided air be excluded, it is not turned blue by ammonia, which seems to show that the metal is in the state of protoxide.—*Edinburgh Philosophical Journal*, i. 24.

Sulphite of Copper may be obtained by passing sulphurous acid into water through which oxide of copper is diffused. Small red crystals are formed, composed of protoxide of copper and sulphurous acid.—CHEVREUL, *Annales de Chimie*, lxxxiii. 181.

When sulphite of potassa is added to nitrate of copper a precipitate falls, which assumes the form of red and yellow crystals. The former are sulphite of copper; the latter a triple *sulphite of potassa and copper*.—CHEVREUL.

Hyposulphate of Copper is formed by adding a solution of persulphate of copper to one of hyposulphate of baryta; it crystallizes in small prisms, very soluble in water, but insoluble in alcohol, and slightly efflorescent.

Persulphate of Copper—*Roman Vitriol*—*Blue Vitriol*.—This salt is formed by dissolving peroxide of copper in diluted sulphuric acid. It crystallizes in rhomboidal prisms of a fine blue colour, doubly refractive, and soluble in about 4 parts of water at 60°, and in 2 parts at 212°. It may also be formed by boiling copper filings in sulphuric acid; a process which furnishes abundance of sulphurous acid, but which is not generally had recourse to, to produce sulphate of copper. It is made upon a large scale, by exposing roasted sulphuret of copper to air and moisture, and thus obtained, is impure, containing iron, and often zinc: it is the common *blue vitriol* of commerce. It is also obtained in large quantities, and very pure, in certain processes afterwards to be described for refining gold and silver; and it is occasionally prepared by dissolving in sulphuric acid a submuriate of copper manufac-

tured for the purpose. When heated, it loses water of crystallization, and at a higher temperature sulphuric acid is evolved, unmixed with sulphurous acid, as in the case of the decomposition of protosulphate of iron, and peroxide of copper remains. It is the *Vitriol* or *Salt of Venus* of the alchymists. When crystallized it contains 10 proportionals of water, and consequently its composition will stand thus :—

1	proportional of peroxide of copper	.	.	= 80
2	„ sulphuric acid (40 × 2)	.	.	= 80
10	„ water (9 × 10)	.	.	= 99
				<hr/>
				259

Sulphate of copper is chiefly employed as a source of several blue and green colours. It has also been used to prevent smut in corn, by steeping the grain in a dilute solution of the salt. (*Quar. Jour.* xvi. 156.) In medicine, it is resorted to as a powerful emetic; and in very minute doses, as a tonic. It is also a valuable external application.

There appears to be no *protosulphate* of copper, for when protoxide of copper is digested in dilute sulphuric acid, metallic copper is separated, and a solution of the peroxide obtained.

By cautiously adding ammonia to a solution of the foregoing salt, a *subpersulphate of copper* is precipitated, consisting of 160 oxide + 40 acid = 200. The same compound is also formed by adding carbonate of lime to a solution of persulphate of copper; an effervescence takes place, and an insoluble blue subpersulphate is precipitated. The alkalis precipitate hydrated peroxide from the solution of the persulphate, and excess of ammonia forms a *triple sulphate of ammonia and copper*. The same compound is formed by triturating carbonate of ammonia with crystals of sulphate of copper. It is the *cuprum ammoniatum* of the *Pharmacopœia*.

Sulphate of Copper and Potassa is a triple salt formed by digesting peroxide of copper in bisulphate of potassa. It crystallizes in rhomboids of a pale blue colour, and consists of one proportional of sulphate of potassa, one of persulphate of copper, and six of water.

Phosphorus and Copper form a gray brittle phosphuret. It

is most easily made by dropping pieces of phosphorus on red-hot copper wire. It is more fusible than copper. Its specific gravity is 7.12. Pelletier found it composed of 100 copper + 20 phosphorus, numbers which nearly agree with 1 proportional of copper = 64 + 1 proportional of phosphorus = 12 = 76 phosphuret of copper.

Neither the *hypophosphite* nor *phosphite of copper* have been examined.

Phosphate of Copper may be formed by mixing solution of sulphate of copper with phosphate of soda; it is a bluish green insoluble powder, composed, as would appear from Mr. Che-
nevix's analysis (*Phil. Trans.* 1803), of

1	proportional of peroxide of copper	.	.	.	= 80
2	„ phosphoric acid (28 × 2)	.	.	.	= 56
1	„ water	.	.	.	= 9
					<hr/>
					145

Native Phosphate of Copper has been found near Cologne. It is of a green colour, and forms small rhomboidal crystals. A specimen, analysed by Mr. Lunn (*Annals of Phil.* iii. 182), afforded

Phosphoric acid	21.687
Peroxide of copper	62.847
Water	15.454
					<hr/>
					100.000

It may, therefore, be regarded as a *subperphosphate of copper*, for these numbers nearly correspond to

1	proportional of peroxide	.	.	.	= 80
1	„ phosphoric acid	.	.	.	= 28
2	„ water (9 × 2)	.	.	.	= 18
					<hr/>
					126

Seleniuret of Copper is formed by heating copper filings with selenium: they act with intense ignition, and a black brittle compound results.

Carbonate of Copper, artificially prepared, by adding carbonate of potassa to sulphate of copper and drying the precipitate, is a green compound, insoluble in water, consisting, according to Mr. R. Phillips, of

1	proportional of	peroxide of copper	.	.	=	80
1	"	carbonic acid	.	.	=	22
1	"	water	.	.	=	9
						<hr/>
						111

It is, therefore, a *subpercarbonate*. Copper, exposed to damp air, becomes incrustated with this compound. Exposed to heat, it loses water and carbonic acid, and leaves the peroxide. In order to heighten the green tint for which this compound is esteemed as a pigment, it should be repeatedly washed with boiling water. There is a fine blue cupreous preparation, called *Refiners' Verditer*, principally made by silver refiners. It consists, according to Mr. R. Phillips, of 3 proportionals of oxide, 4 of carbonic acid, and 2 of water. (*Quarterly Journal of Science and Arts*, vol. iv. p. 277.) There is a very inferior pigment, also called Verditer, which is a mixture of subsulphate of copper and chalk. According to Pelletier, a good verditer may be obtained as follows: add a sufficient quantity of lime to nitrate of copper to throw down the hydrated oxide; it gives a greenish precipitate that is to be washed and nearly dried upon a strainer; then incorporate with it from 8 to 10 *per cent.* of fresh lime, which will give it a blue colour, and dry it carefully. According to Mr. Chenevix, the alkaline carbonates dissolve a portion of the peroxide of copper, and form triple salts.

Native Carbonate of Copper is found of a green and blue colour. The former, or *Malachite*, is found in various forms, but never regularly crystallized, the octoëdral variety being a pseudo-crystal derived from the decomposition of the red oxide. This mineral occurs in the greatest beauty in the Uralian mountains of Siberia; it is rarely found in Cornwall. It is of various shades of green, and often cut into small slabs, or used as beads and broach-stones. The pulverulent variety has been termed *chrysocolla* and *mountain green*.

The *blue carbonate* is found in great perfection at Chessy near Lyons; also in Bohemia, Saxony, &c. It occurs crystallized in rhomboids and imperfect octoëdra: it also is found in small globular masses; massive; and earthy. The earthy variety is sometimes called *copper azure* or *mountain blue*.

The *Diophtase* or *Emerald Copper* is a very rare mineral, hitherto found only in Siberia, associated with malachite. It

consists, according to Lowitz, of oxide of copper, silica, and water.

Borate of Copper.—Solution of borax, poured into sulphate of copper, produces a bulky pale green precipitate of borate of copper.

Ferrocyanate of Copper is a brown compound, obtained by adding ferrocyanate of potassa to a dilute solution of sulphate or nitrate of copper. Mr. Hatchett has recommended this substance as a brown pigment.

The cupreous salts are nearly all soluble in water, and of a blue or green colour. Ammonia produces a compound of a very deep blue, when added in excess to these solutions; hydrosulphuret of ammonia forms a black precipitate: and a plate of iron plunged into a liquid salt of copper precipitates metallic copper. Ferrocyanate of potassa is also an excellent test of the presence of copper; it produces a brown cloud in solutions containing the minutest portion of the peroxide.

Alloys of Copper.—Many of the alloys of copper are important. With gold it forms a fine yellow ductile compound, used for coin and ornamental work. Sterling or standard gold consists of 11 gold + 1 copper. The specific gravity of this alloy is 17.157. With silver it forms a white compound, used for plate and coin. Lead and copper require a high red heat for union; the alloy is gray and brittle.—See GOLD and SILVER.

Of the alloys of copper with the preceding metals the most important are brass and bell-metal. It forms white compounds with potassium and sodium; a reddish alloy with manganese; and a gray one with iron.

Brass is an alloy of copper and zinc. The metals are usually united by mixing granulated copper with calamine and charcoal: the mixture is exposed to heat sufficient to reduce the calamine and melt the alloy, which is then cast into plates. The relative proportions of the two metals vary in the different kinds of brass; there is usually from 12 to 18 *per cent.* of zinc. Brass is very malleable and ductile when cold; and its colour and little liability to rust recommend it in preference to copper for many purposes of the arts. According to M. Sage, a very beautiful brass may be made by mixing 50 grains of oxide of copper, 100 of calamine, 400 of black flux, and 30 of charcoal powder; melt these in a crucible till the blue flame

is no longer seen round the cover ; and, when cold, a button of brass is found at the bottom, of a golden colour, and weighing one-sixth more than the pure copper obtained from the above quantity of oxide.

The *analysis of brass* may be performed by solution in nitric acid ; add considerable excess of solution of potassa and boil, which will dissolve the oxide of zinc and leave that of copper ; wash the latter, and dry and heat it to redness : 125 parts indicate 100 of copper. The zinc in the filtered alkaline solution may be precipitated by carbonate of soda, having previously added a small excess of muriatic acid ; wash this precipitate, dry it, and expose it to a red heat ; it is then oxide of zinc, 123 parts of which indicate 100 of metal.

But as, in the above process, the whole of the oxide of zinc is not easily removed by the alkaline solution, Mr. Keates recommends the following as a preferable operation : dissolve the brass in dilute nitric acid, evaporate to dryness, and redissolve in excess of dilute sulphuric acid ; filter, to separate sulphate of lead, if any be present ; dilute the solution, heat it to its boiling point, and introduce three polished cylinders of iron, each about an inch long and a fourth of an inch diameter ; continue the boiling till the solution becomes colourless, and when tested by a clean plate of iron shows no trace of copper. Filter the solution while hot, and wash the precipitated copper first with very dilute sulphuric acid, and afterwards with boiling water ; dry it, and fuse it into a button in a crucible covered with charcoal powder. Boil the filtered solution with the addition of some nitric acid to peroxidize the iron, and nearly neutralize by carbonate of soda ; then add excess of ammonia, to throw down the peroxide of iron, which separate by filtration. Add muriatic acid to the filtered ammoniacal solution, evaporate to dryness, and heat in a silver crucible to drive off muriate of ammonia ; dissolve the residue in muriatic acid, and precipitate by excess of carbonate of soda ; wash, dry, and ignite the precipitate, which reduces it to the state of oxide of zinc.

Tutenag is said to be an alloy of copper, zinc, and a little iron ; and *Tombac*, *Dutch gold*, *Similor*, *Prince Rupert's metal*, and *Pinchbeck*, are alloys containing more copper than exists in brass, and consequently made by fusing various pro-

portions of copper with brass. According to Wiegleb, *Manheim gold* consists of 3 parts of copper and 1 of zinc. A little tin is sometimes added, which, though it may improve the colour, impairs the malleability of the alloy.

An alloy of 576 parts of copper, 59 of tin, and 48 of brass, is equal to brass in hardness, and may be worked with the same facility; it was used by Mr. Bate for the new standard measures, as being less liable than brass to oxidizement.—*Phil. Trans.* 1826, part ii. p. 9.

Speculum Metal is an alloy of copper and tin, with a little arsenic; about 6 copper, 2 tin, 1 arsenic. On this subject the reader is referred to Mr. Edwards's experiments.—Nicholson's *Journal*, 4to. iii. Mr. Little recommends 32 parts of best bar copper, 4 of brass pin wire, $16\frac{1}{2}$ of tin, and $1\frac{1}{4}$ of arsenic. He first melts the brass, and adds about its weight of tin; when this is cold, the copper, previously fused with black flux, is added; then the remainder of the tin; and, lastly, the arsenic. This mixture is granulated, and again fused for casting.

Bell Metal and *Bronze* are alloys of copper and tin; they are harder and more fusible, but less malleable than copper; the former consists of 3 parts of copper and 1 of tin; the latter of from 8 to 12 of tin with 100 of copper. A little zinc is added to small shrill bells. Bronze is softened in texture when heated and then suddenly cooled; heating afterwards hardens it: these effects are the reverse of those produced upon steel.

The analysis of alloys of tin and copper may be performed by digestion in nitric acid, which dissolves the copper and converts the tin into insoluble peroxide, which, when washed and dried, consists of 100 tin + 27 oxygen. The cupreous solution may be decomposed by potassa, and the pure peroxide of copper indicates the quantity of that metal, as in the analysis of brass.

Vessels of copper used for culinary purposes are usually coated with tin, to prevent the food being contaminated with copper. Their interior surface is first cleaned, then rubbed over with sal-ammoniac. The vessel is then heated, a little pitch spread over the surface, and a bit of tin rubbed over it, which instantly unites with and covers the copper.

Section XIV. LEAD.

THE natural compounds of this metal are very numerous. The most important is the sulphuret, from which the pure metal is chiefly procured. Lead is also found combined with carbonic, sulphuric, phosphoric, arsenic, molybdic, and chromic acids, and with oxygen and chlorine. To obtain lead perfectly pure, it may be dissolved in nitric acid; the solution evaporated to dryness; the dry mass redissolved in water and crystallized; these crystals heated strongly with charcoal afford the metal quite pure.

Lead appears to have been known in the earliest ages of the world. Its colour is bluish-white. It is remarkably flexible and soft, and leaves a black streak on paper. It melts at 600° , and, by the united action of heat and air, is readily converted into an oxide. Its specific gravity is 11.4. At common temperatures it undergoes little change by mere exposure to air, but it is slowly corroded by the joint agency of air and water. Exposed upon ignited charcoal to a current of oxygen gas, it boils and burns with a blue flame, throwing off dense yellow fumes of oxide. The alchymists gave this metal the name of *Saturn*.

Oxides of Lead.—There are three oxides of lead. The *protoxide* is the basis of the salts; it may be obtained pure by heating the nitrate of lead to redness in a vessel with a small orifice, till the whole of the acid is expelled. It is insipid and insoluble in water, of a pale yellow colour, and, when fused, crystallizes on cooling in irregular scales. It is volatile at a bright red heat. It is soluble in solutions of potassa and soda, and sparingly so in lime and baryta water; and when in fusion, it readily dissolves several of the earthy bodies, and of the common metallic oxides; hence the use of lead in *cupellation*. This oxide is known in commerce under the name of *massicot*; or when vitrified, as obtained by calcining lead upon a large scale, it is called *litharge*. When melted lead is exposed for a time to the air, it becomes encrusted with a gray pellicle, which, on removal, is succeeded by another, and so on until the whole is converted into a

greenish-gray powder, consisting of a mixture of the protoxide with metallic lead.

The number 104 is the equivalent of lead, and the protoxide consists of

1	proportional of lead	=	104
1	„	oxygen	=	8
									<hr/>
Equivalent of protoxide of lead									= 112

If the protoxide be exposed to heat and oxygen, it gradually acquires a bright red colour, and is known under the name of *minium* or *deutoxide* of lead. This oxide, when exposed to nitric acid, is resolved into protoxide, which is dissolved, and into *peroxide*, which is insoluble.

When minium is heated to redness it gives out oxygen, and is converted into protoxide. It does not form salts. It consists of

1	proportional of lead	=	104
1½	„	oxygen	=	12
									<hr/>
Equivalent of deutoxide of lead									= 116

The minium or *red lead* of commerce generally contains a proportion of protoxide and of sulphate, with traces of chloride of lead and silica. To succeed in obtaining it of a fine red tint, it requires to be manufactured in quantities, and with several precautions. The method employed in Derbyshire is described in Watson's *Chemical Essays*, vol. iii. p. 338.

Peroxide of Lead is obtained in the form of an insoluble brown powder by digesting minium in nitric acid. At a red heat it gives off oxygen, and is converted into protoxide. Digested in liquid ammonia, a mutual decomposition takes place, and water and nitrate of lead are formed. Triturated with a fifth of its weight of sulphur, it inflames spontaneously. With muriatic acid, it furnishes chlorine and chloride of lead. It readily absorbs sulphurous acid, and forms with it sulphate of lead. According to Vogel, it becomes red hot when acted upon by pure sulphurous acid gas. It consists of

1	proportional of lead	=	104
2	„	oxygen	=	16
									<hr/>
Equivalent of peroxide of lead									= 120

A substance, supposed to be *native minium*, has been found in some of the Saxon and French lead mines; also in Yorkshire.

Lead and Chlorine—Chloride of Lead.—When laminated lead is heated in chlorine, the gas is absorbed, and a chloride of lead results. (J. Davy, *Phil. Trans.*, 1812.) The same substance is obtained by adding muriatic acid to nitrate of lead; it is white and fusible, and, on cooling, forms a hornlike substance (*plumbum corneum*). It volatilizes at a high temperature. It dissolves in 30 parts of water at 60°, and in 22 at 212°, separating, as its solution cools, in small anhydrous acicular crystals, unchanged by exposure to air, and of a sweetish taste. It dissolves in dilute nitric acid; it is insoluble in alcohol.

This substance is sometimes prepared by acting upon a solution of common salt by litharge; solution of soda and chloride of lead are formed; the insoluble residue when fused is known under the name of *patent yellow*; it appears to be a compound of oxide and of chloride of lead; for when treated by nitric acid, it forms nitrate of lead, and a portion of chloride separates.

Native Chloride of Lead has been found in Derbyshire and in Bavaria, crystallized in quadrangular prisms of a greenish yellow colour.

Chlorate of Lead is obtained by digesting the protoxide in chloric acid; it separates by slow evaporation, in white crystalline flakes of a very sweet taste. When heated, it gives out oxygen, and becomes a chloride.

Iodide of Lead, formed by heating leaf-lead with iodine, is a yellow compound. It is also formed by adding hydriodic acid or hydriodate of potassa to solution of nitrate of lead; it then falls in the form of a bright yellow powder, sparingly soluble in boiling water, and separating, as the solution cools, in beautiful brilliant flakes. It is soluble in caustic potassa.

An insoluble *Iodate of Lead* is thrown down on adding iodate of potassa to any of the soluble salts of lead. It redissolves in excess of the acid.

Bromide of Lead is precipitated from a solution of lead by hydrobromic acid; it is fusible, and concretes on cooling into a yellow mass. When first precipitated, it is decomposed by sulphuric and nitric acids; but when fused, it requires boiling sulphuric acid to produce that effect.

Bromate of Lead is thrown down in the form of a white powder, by adding bromic acid to a dilute solution of nitrate of lead.

Fluoride of Lead is almost insoluble, and obtained by adding hydrofluoric acid to nitrate of lead, when it falls in the form of a white powder, soluble in nitric and muriatic acids, by which, when evaporated, it is decomposed. Ammonia converts the fluoride into a *subfluoride* of lead, which is more soluble than the former.

Nitrate of Lead is obtained by dissolving the metal, not in excess, in dilute nitric acid, and evaporation. The salt crystallizes in tetraëdra and octoëdra, which have a specific gravity = 4; they are white, translucent, and of a styptic taste, containing no water of crystallization. It is soluble in 8 parts of water at 212°, and insoluble in alcohol. The alkalis throw down a white hydrated protoxide of lead from the solution of this salt. The proportion of water contained in this hydrate has not been determined. This salt consists of

1	proportional of oxide of lead	= 112
1	„ nitric acid	= 54
							<hr/>
	Equivalent of nitrate of lead	= 166

Subnitrate of Lead may be formed by boiling a mixture of equal weights of nitrate and protoxide of lead in water, filtering while hot, and setting it by to crystallize; it forms pearly crystals, of a sweet astringent taste. (Chevreul, *Ann. de Chim.*, lxxxii.) It consists of

2	proportionals of oxide of lead (112 × 2)	= 224
1	„ nitric acid	= 54
							<hr/>
							278

Chevreul and Berzelius have described three *nitrites* of lead, but their composition appears doubtful. (*Ann. de Chim.* lxxxiii. and lxxxviii.) A detailed account of them is given by Berzelius (*Lehrbuch*, ii.), and by Dr. Thomson,—*System*, ii. 578.

Sulphuret of Lead may be formed artificially by fusion. Its lustre and colour much resemble pure lead, but it is brittle.

Its specific gravity is 7.5, and it consists of

1	proportional of lead	= 104
1	„ sulphur	= 16
							<hr/>
	Equivalent of sulphuret of lead	= 120

Native Sulphuret of Lead, or *Galena*, is the principal source of the vast commercial demands of the metal. It occurs massive and crystallized, chiefly in the older secondary rocks. Its primitive form is the cube, of which there are several modifications, and among them the octoëdron. It often contains traces of silver, and sometimes in such quantity as to render it worth separating, which is effected by exposing the roasted sulphuret to the action of heat and air in shallow earthen dishes; the lead becomes oxidized and converted into litharge, while the silver is left pure, in consequence of its power of resisting the influence of heat and air. This process is called *cupellation*. The litharge is afterwards reduced by fusion with charcoal.

The reduction of galena upon a large scale is a sufficiently simple process. The picked ore, after having been broken and washed, is roasted in a reverberatory fire, the temperature being such as to soften but not fuse it. During this operation it is raked till the fumes of sulphur are dissipated, when it is brought into perfect fusion; the lead, reduced by the fuel, sinks to the bottom, and is run out into oblong moulds called *pigs*; the scoriæ are again melted, and furnish a portion of less pure metal. The mines of Great Britain afford an annual produce of about 48,000 tons of smelted lead, of which nearly the whole is obtained from the sulphuret. There is a specular variety of galena, called in Derbyshire *slickensides*; and which, when touched by the miner's pick, often splits asunder with a kind of explosion.

When sulphuretted hydrogen is added to solutions of lead, a black precipitate falls, which is a hydrosulphuretted oxide of lead; and which, by drying, loses water, and when fused, furnishes sulphuret of lead. The solutions of lead precipitated by any of the compounds of bisulphuretted hydrogen afford brown precipitates, which probably contain more sulphur than the black. Lead has already been adverted to as a most delicate test of sulphuretted hydrogen. (Vol. i. p. 266.)

Hyposulphite of Lead is precipitated in the form of a white powder, by adding solution of nitrate of lead to hyposulphite of potassa. At 212° it becomes dark coloured, and at a higher temperature burns like tinder. Distilled in close vessels, it gives out sulphurous acid, and is converted into sulphuret and

sulphate of lead. It is composed, according to Herschel, of 70.30 protoxide of lead + 29.70 hyposulphurous acid. These numbers correspond to 1 proportional of oxide of lead = 112 + 2 proportionals of hyposulphurous acid = 48.

Sulphite of Lead may be obtained by digesting yellow oxide of lead in sulphurous acid; or by adding sulphurous acid or sulphite of potassa to nitrate of lead. It is white, insoluble, and tasteless. When heated it loses sulphurous acid. It is converted by nitric acid into sulphate of lead. It disengages sulphurous acid when acted upon by muriatic and by sulphuric acid. It consists of

1 proportional of oxide of lead	.	.	.	=	112
1 „ sulphurous acid	.	.	.	=	32
Equivalent of sulphite of lead	.	.	.	=	144

Hyposulphate of Lead is formed by digesting carbonate of lead in hyposulphuric acid, filtering and evaporating. It forms soluble crystals, which contain 4 proportionals of water.

Sulphate of Lead.—Cold sulphuric acid has no action upon metallic lead; but when the metal is boiled in concentrated sulphuric acid, sulphurous acid is evolved, and a white sulphate of lead is formed. It is so insoluble, that it may be formed by adding dilute sulphuric acid, or an alkaline sulphate, to a solution of nitrate of lead. Dr. Thomson found, that after having been dried at a temperature of 400°, it might be heated to redness in a platinum crucible without losing weight. Heated on charcoal by the blowpipe, it is decomposed and reduced. Sulphate of lead is insoluble in alcohol and nearly so in nitric acid; muriatic acid partially decomposes it. It is sparingly soluble in excess of sulphuric acid, and separates from it in small prismatic crystals. It is an anhydrous salt. It consists of

1 proportional of oxide of lead	.	.	.	=	112
1 „ sulphuric acid	.	.	.	=	40
Equivalent of sulphate of lead	.	.	.	=	152

Native Sulphate of Lead is found in Anglesea, and in Scotland, crystallized in prisms and in octoëdra.

Phosphuret of Lead may be formed by dropping phosphorus into melted lead. It is of the colour of lead, and soon tarnishes.

Hypophosphite of Lead has not been examined.

Phosphite of Lead was prepared by Berzelius by mixing muriate of lead with phosphite of ammonia. It is white, tasteless, and insoluble, and appears to consist of 1 proportional of oxide of lead = 104.5 + 1 proportional of phosphorous acid = 18.5.

Phosphate of Lead is formed by mixing solutions of nitrate of lead and phosphate of soda, or phosphoric acid. It is yellowish white; insoluble in water; soluble in fixed alkaline solutions, and in nitric acid. It is decomposed by sulphuric acid, and by hot muriatic acid. It fuses before the blowpipe, and crystallizes on cooling. It consists of

1 proportional of oxide of lead	.	.	.	= 112
1 " phosphoric acid	.	.	.	= 28
Equivalent of phosphate of lead	.	.	.	= 140

Berzelius has described a *subphosphate*, a *superphosphate*, and a *nitrophosphate of lead*.—*Annales de Chim. et Phys.* ii.

Native Phosphate of Lead has been found in the mines of Cumberland, Durham, Yorkshire, and of Wanlock Head, in Scotland. Its colour is various shades of green, yellow, and brown. Its primitive form is a rhomboid, but it usually occurs in six-sided prisms. It is semi-transparent and brittle.

Seleniuret of Lead and *Seleniate of Lead* have already been mentioned at page 289, vol. i. The seleniuret is formed artificially by heating its components: it is difficultly fusible, and of a metallic lustre; heated by the blowpipe, it is gradually converted into a seleniate.

Carburet of Lead.—The compounds described under this name are probably mixtures of finely divided metallic lead and charcoal.

Carbonate of Lead.—When an alkaline carbonate is added to nitrate of lead, a white precipitate of carbonate of lead falls: it is tasteless, insoluble in water, but soluble in fixed alkaline solutions. It is employed as a white paint, under the name of *white lead* or *ceruse*, and is usually prepared by exposing sheet lead to the action of the vapour of vinegar, or by decomposing acetate of lead by a carbonate. It consists of

1 proportional of oxide of lead	.	.	.	= 112
1 " carbonic acid	.	.	.	= 22
Equivalent of carbonate of lead	.	.	.	= 134

Native Carbonate of Lead is one of the most beautiful of the metallic ores: it occurs crystallized and fibrous, the former transparent, the latter generally opaque. It is soft and brittle, and occasionally tinged green with carbonate of copper, or gray by sulphuret of lead. The octoëdron is its primitive form: it also occurs prismatic and tabular. It has been found in Cumberland and Durham, and the acicular variety of great beauty in Cornwall.

Ferrocyanate of potassa produces a white precipitate when added to the soluble salts of lead, which is a *ferrocyanate of lead*.

Borate of Lead is precipitated in the form of a white powder, when borate of soda is mixed with nitrate of lead.

The *soluble salts of lead* have a sweetish austere taste, and are characterized by the white precipitate produced by ferrocyanate of potassa, black by sulphuretted hydrogen, the deep brown by hydrosulphuret of ammonia, the yellow by hydriodate of potassa, and the white by sulphuric acid and the soluble sulphates.

The *salts insoluble in water* are dissolved by soda and potassa, and by nitric acid, when the metal is rendered manifest by sulphuretted hydrogen and other tests. Heated by the blowpipe upon charcoal they afford a button of metal.

The *Alloys of Lead* with the preceding metals are not important, if we except that which it forms with tin. Common *pewter* consists of about 80 parts of tin and 20 of lead. Equal parts of lead and tin constitute *plumbers' solder*; and what is termed *pot-metal* is an alloy of lead and copper.

In analyzing these alloys, 100 grains in filings may be boiled to dryness in two ounces of nitric acid, water poured upon the residue, and filtered; the peroxide of tin remains in the filter, and the nitrate of lead, which passes through in solution, may be converted into sulphate by adding sulphate of soda. 152 grains of sulphate of lead dried at a red heat, indicate 104 of metal; and 74 grains of washed peroxide of tin are equivalent to 58 grains of metallic tin.

With potassium lead forms a brittle and very fusible alloy: with sodium the compound is equally brittle but less fusible. When exposed to air these alloys suffer decomposition in consequence of the oxidizement of the alkaline bases. The alloy

of lead and manganese has not been examined. When lead is fused with iron, two alloys are obtained; that at the bottom of the crucible consisting of lead with a little iron; while the superficial portion is iron with a little lead (Guyton Morveau, *Ann. de Chim.* lvii.) With zinc, lead forms a hard ductile alloy.

Section XV. ANTIMONY.

THIS metal is found *native* in Sweden, in France, and in the Hartz; but its principal ore is the *sulphuret*, which is found massive and crystallized, and of which there are several varieties. The most common is the *radiated*, which is of a gray colour, brittle, and frequently crystallized in four and six-sided prisms. This ore may be decomposed, and the pure metal obtained from it, by the following process: Mix three parts of the powdered sulphuret with two of crude tartar, and throw the mixture by spoonfuls into a red-hot crucible; then heat the mass to redness, and a button will be found at the bottom of the crucible, which is the metal as it commonly occurs in commerce, and is nearly pure. Reduce this button to fine powder, and dissolve it in nitro-muriatic acid; pour this solution into water, which will occasion the precipitation of a white powder, which is to be washed and mixed with twice its weight of tartar, and exposed to a dull red heat in a crucible. The button now obtained is pure antimony.

Antimony is of a silvery white colour, brittle and crystalline in its ordinary texture. It fuses at about 800° , and is volatile at a very high heat. Its specific gravity is 6.712. (Hatchett, *Phil. Trans.* 1803.) Placed upon ignited charcoal, under a current of oxygen gas, antimony burns with great brilliancy, throwing off its oxide in the form of a dense yellow smoke.

Antimony and Oxygen.—Much difference of opinion has prevailed among chemists respecting the number and composition of the definite oxides of antimony: it is probable that there are at least three, of which one only, the protoxide, is

salifiable. I long ago found that the oxygen in the protoxide (as contained in emetic tartar) was to that in the peroxide (obtained by the action of nitric acid upon the metal) as *one to two*; and I considered the former as composed of about 42 metal and 8 oxygen, and the latter of 42 metal and 16 oxygen. Dr. John Davy's researches on the composition of the chlorides, gives, as the equivalent of antimony, a number approaching to 45. If we assume 44 as its equivalent, the following will be the composition of the oxides of antimony:—

1	proportional of antimony	.	.	= 44	} = 52 Protoxide.
1	„ oxygen	.	.	= 8	
1	proportional of antimony	.	.	= 44	} = 56 Deutoxide.
1½	„ oxygen	.	.	= 12	
1	proportional of antimony	.	.	= 44	} = 60 Peroxide.
2	„ oxygen (8 × 2)	.	.	= 16	

The *Protoxide of Antimony* is thus obtained:—To 200 parts of sulphuric acid add 50 parts of powdered metallic antimony. Boil the mixture to dryness, wash the dry mass, first in water, and then with a weak solution of carbonate of potassa; a white powder remains, which, when thoroughly washed with hot water, is *protoxide of antimony*. It may also be procured by dissolving antimony in muriatic acid, pouring the solution into water, and washing the white precipitate with solution of carbonate of potassa or of soda. This oxide may also be obtained by adding ammonia to solution of tartrate of antimony and potassa, heating the mixture, and washing the precipitate in large quantities of boiling water. It is thus procured in the form of a heavy white powder. This process is directed in the *Pharmacopœia*.

This protoxide exists in all the active antimonial preparations; in emetic tartar, kermes, glass of antimony, golden sulphuret, &c. It is fusible and volatile at a red heat, undergoing no change in close vessels; but if air be present, it undergoes a kind of combustion, and passes into the state of deutoxide. It is decomposed by sulphur and charcoal; and when acted on by nitric acid, is converted into peroxide; if heated with chlorate of potassa it deflagrates and also becomes peroxidized; it is very soluble in muriatic acid, and readily forms emetic tartar when boiled in solution of tartrate of potassa. When recently precipitated, and digested in caustic potassa, it

is partly converted into a gray powder, which is a true compound of the oxide and the alkali, very difficultly soluble. A similar combination may be obtained with soda and ammonia.

When metallic antimony in fusion is exposed to a bright red heat, it is converted into an oxide, which appears to be the protoxide, and which condenses in long and delicate needles when sublimed. It was formerly called *argentine flowers of antimony*.

Deutoxide of Antimony, or *Antimonious Acid*, is the result of the above mentioned combustion of the protoxide. It is also obtained by exposing the peroxide to a red heat. It is white, but assumes a yellow colour when heated; fixed and infusible in the fire, insoluble in nitric acid, and nearly so in sulphuric acid. It readily combines with potassa by fusion, and the resulting compound (*antimonite of potassa*) dissolves in water, and furnishes, upon the addition of an acid, a white precipitate of *hydrated deutoxide*, which, when thoroughly edulcorated, has the property of reddening litmus.

Peroxide of Antimony, or *Antimonic Acid*, is procured by acting for a considerable time upon the powdered metal, by excess of hot nitric acid, and exposing the product to a heat of about 500°. The *diaphoretic antimony* and *Bezoar mineral* of old *Pharmacopœia* consisted of this oxide, which, compared with the protoxide, is nearly inert.

Peroxide of antimony is white, tasteless, and insoluble in water. It neither fuses nor volatilizes at a bright red heat, but when exposed to the flame of a spirit-lamp urged by a blowpipe, it passes off slowly in white fumes, being partially reduced by the hydrogen of the flame. It does not decompose the alkaline carbonates in the humid way, but at a red heat it expels their carbonic acid, and combines with the base. It dissolves in the liquid caustic alkalis, and in muriatic acid when in the state of hydrate; but after exposure to a red heat becomes of extremely difficult solubility.

Peroxide of antimony may also be obtained by deflagrating a mixture of four parts of nitre, and one of powdered antimony, and washing the residue with nitric acid and water; or, by dissolving antimony in nitro-muriatic acid, and pouring the solution into water: it is thus, when edulcorated, a hydrated peroxide, and may be dried nearly at a red heat: at somewhat

higher temperatures it loses oxygen and passes into deutoxide.

Antimoniate of Ammonia is formed by digesting the acid in ammonia. On evaporation a *super-antimoniate of ammonia* is obtained in the form of a white powder.

Antimoniate of Potassa is contained in the white powder obtained by igniting nitre and antimony. It dissolves in hot water, and this solution produces precipitates of insoluble antimoniates in several other metallic solutions.

Antimony and Chlorine combine in two proportions. The powdered metal takes fire when thrown into gaseous chlorine, and a compound, at first liquid, but afterwards concreting, is formed. A similar compound may also be produced by the distillation of one part of powdered antimony with two and a half of perchloride of mercury; or by dissolving the protoxide of antimony in muriatic acid, and evaporating to dryness. The *protochloride* of antimony thus obtained, is a soft solid at common temperatures, but becomes liquid by a gentle heat, and crystallizes as it cools. It is the *butter of antimony* of old writers. It deliquesces by exposure to air; and is a powerful caustic. When water is added to the protochloride of antimony, a mutual decomposition ensues, and hydrated protoxide of antimony, formerly called *Algarotti's powder*, or *mercurius vitæ*, and muriatic acid, result. It consists of

1 proportional of antimony	= 44
1 „ chlorine	= 36
						<hr/>
Equivalent of protochloride of antimony	.					= 80

Perchloride of Antimony is formed by passing dry chlorine over heated antimony. It is a volatile transparent liquid, which emits copious fumes when exposed to air. When dropped into water a hydrated peroxide of antimony falls, and muriatic acid is formed. (Rose, *Ann. of Phil.*, N. S., x.) It consists of

1 proportional of antimony	= 44
2 „ chlorine (36 × 2)	= 72
						<hr/>
Equivalent of bichloride of antimony	.					= 116

Chlorate of Antimony has not been examined.

Iodide of Antimony is of a dark colour; acted upon by water, it produces hydriodic acid and protoxide of antimony.

Iodate of Antimony is unknown.

Bromide and Fluoride of Antimony have not been examined.

Nitric acid acts powerfully on metallic antimony, and if mixed with it in fine powder, will sometimes cause its inflammation. The metal becomes peroxide, and scarcely an appreciable portion is retained in solution. As in some other cases of the vehement decomposition of nitric acid, ammonia is produced, which may be rendered sensible by pouring potassa on the white magma that results, and by which the nitrate of ammonia is decomposed.

Protoxide of antimony, digested in dilute nitric acid, produces a difficultly soluble salt, which separates in white scaly crystals, and which appears to be a *nitrate of antimony*, but I have not particularly examined it.

Nitro-muriatic acid readily dissolves antimony, and forms an orange-coloured solution, which is decomposed by the addition of water. Iron or zinc immersed into this solution throws down a black powder, which, according to Thenard, is pyrophoric.

Sulphuret of Antimony is easily formed by fusing the metal with sulphur. Its colour is dark gray and metallic; its specific gravity 4.36. It closely resembles the native sulphuret. It consists of

1 proportional of antimony	.	.	.	= 44
1 „ sulphur	.	.	.	= 16
				<hr/>
Equivalent of sulphuret of antimony	.	.	.	= 60

Sesquisulphuret of Antimony is formed when sulphuretted hydrogen is passed through the muriatic solution of deutoxide of antimony; and when a solution of the peroxide is similarly decomposed, a *bisulphuret of antimony* is precipitated. (Rose, *Ann. of Phil.*, N. S., x.)

When sulphuret of antimony is exposed under a muffle to a dull red heat, it gradually loses sulphur, and absorbs oxygen, being converted into a gray powder, which consists of a mixture of protoxide of antimony and sulphuret. If the heat be increased, this fuses into a transparent substance of a yellow or

brown colour, formerly called *glass of antimony*. Its composition is variable ; it generally contains about 85 *per cent.* of protoxide and 15 of sulphuret. In that which is imported for pharmaceutical purposes, from Germany and Holland, there is usually a portion of siliceous earth, and it is sometimes adulterated with oxide of lead. This fraud is easily detected by digesting the finely-powdered glass in hot nitric acid, diluting the solution and filtering. The filtered liquor gives a white precipitate on the addition of sulphate of soda, if lead is present.

During the formation of glass of antimony, if the heat be raised too high the greater part of the protoxide sublimes in slender crystalline needles ; while another portion, if air be not excluded, passes into the state of deutoxide, and undergoes no further change at a very high temperature.

Compounds of the protoxide with larger quantities of the sulphuret have been termed *saffron of antimony* or *crocus metallorum*, and *liver of antimony*.

Hydrosulphuretted Oxide of Antimony.—This compound has long been known under the name of *kermes mineral* ; it is commonly prepared as follows : Equal parts of sulphuret of antimony and common potash are fused together ; the resulting mass is finely powdered, and boiled in ten times its weight of water. The liquor is filtered while hot ; and, during cooling, it deposits *kermes*. The mother liquor of *kermes* deposits a copious yellowish red precipitate upon the addition of dilute sulphuric acid, which, when washed and dried, is known under the name of *golden sulphur of antimony*. In the *London Pharmacopœia* it is called *antimonii sulphuretum præcipitatum*.

In forming these compounds, the following changes seem to have taken place. The sulphuret of antimony and potassium acts upon the water, a portion of which is decomposed ; hydrosulphuret of potassa is formed, and hydrogen and oxygen unite to the sulphuret of antimony, producing a hydrosulphuretted oxide of that metal (*kermes*), which remains dissolved in the hot alkaline hydrosulphuret, and of which one portion is precipitated as that solution cools. When dilute sulphuric acid is added, the hydrosulphuret of potassa is decomposed, sulphate of potassa is formed, and sulphur and sulphuretted hydro-

gen are liberated ; the sulphur falls in combination with the *kermes*, producing the *golden sulphur*, or sulphuretted hydro-sulphuret.

Dr. Turner considers *kermes* and the golden sulphur as hydrated sulphurets of antimony, and not as hydrosulphuretted oxides ; but their extreme activity as medicines seems to render the existence of protoxide in them probable.

Sulphite of Antimony is an insoluble white salt, obtained by digesting the protoxide in sulphurous acid, or by passing sulphurous acid into protomuriate of antimony.

Sulphate of Antimony is the white saline mass formed by boiling powdered antimony in sulphuric acid. Water resolves it into an insoluble *subsulphate* and a soluble *supersulphate* : the latter may be obtained in small deliquescent acicular crystals by evaporation.

Phosphuret of Antimony is formed by heating together equal parts of oxide of antimony, phosphoric acid, and charcoal. It is white and brittle.

Nothing is known respecting either the *Hypophosphite* or the *Phosphite* of antimony.

Phosphate of Antimony.—When protoxide of antimony is digested in phosphoric acid it is dissolved, but affords no crystallizable salt on evaporation.

In the *London Pharmacopœia* there is a preparation called *pulvis antimonialis*, formed by heating one part of sulphuret of antimony with two of hartshorn shavings. The action of heat upon the sulphuret has already been described. Its effect upon the hartshorn shavings is to destroy the animal matter, leaving little else than phosphate of lime. So that the *pulvis antimonialis* consists essentially of an oxide of antimony, mixed with phosphate of lime. This preparation is usually considered analogous to, if not identical with, *James' Powder*, which, according to Dr. Pearson's analysis (*Phil. Trans.*, 1791), consists of 43 phosphate of lime, and 57 oxide of antimony. Be this as it may, the antimonial powder of the *Pharmacopœia* is an uncertain and ill-contrived preparation : its activity depends upon the proportion of protoxide which it contains ; but the greater part of the protoxide is apt to be volatilized, or converted into deutoxide, of a mixture of which with phosphate of lime, the antimonial powder generally con-

sists. Accordingly, in examining Antimonial Powder from various sources, prepared after the direction of the *Pharmacopæia*, I have found it of variable composition : sometimes it contains deutoxide of antimony only ; sometimes there is a proportion of protoxide ; and in some few cases the powder has consisted chiefly of bone-earth. These differences are referable to the mode of preparing it, but in almost every case, a very large proportion of the protoxide is lost during the process, and I have found it a matter of great difficulty so to conduct it as to obtain, upon the large scale, an uniform product. For medical use I should consider emetic tartar as the only certain and necessary preparation of antimony ; if, however, a compound of the nature of the Antimonial Powder be requisite, one of the best modes of preparing it would be to dissolve certain proportions of protoxide of antimony and phosphate of lime in muriatic acid, precipitate by ammonia, andedulcorate with a large quantity of water. Mr. Chenevix advises for this purpose equal parts of the oxide and phosphate, but such proportion of antimony is too great : I have made an useful Antimonial Powder by dissolving 200 grains of bone-earth and 100 of protoxide of antimony in a measured ounce and a half of muriatic acid, and pouring the solution into a weak solution of ammonia ; the precipitate, when washed, dried, and reduced to a fine powder, weighed 280 grains.

The following method furnishes, in the dry way, a tolerably uniform Antimonial Powder : burn two pounds of hartshorn to a cinder, reduce it to powder, and heat it to a dull redness in an iron pot : then gradually stir into it one pound of powdered sulphuret of antimony, added in successive portions, and continue the same heat as long as fumes arise ; when these cease, the mixture will have a dirty gray colour, and during the operation small crystals of protoxide of antimony will be seen to collect upon its surface when a portion is taken out in an iron spoon. In this gray state it should be put into a covered crucible and heated to intense redness ; a phosphorescent light of a greenish tint is soon perceived, and when this ceases the crucible may be removed from the fire, and its contents when cold reduced to a fine powder, which should be perfectly white.

Neither *carbonate*, *hydrocyanate*, nor *borate* of antimony are known to exist.

The *solutions of antimony* afford orange-coloured precipitates with sulphuretted hydrogen, and some of those which are acid are precipitated when largely diluted with water.

Alloys of Antimony—Antimony forms brittle alloys with the malleable metals. When gold was alloyed with $\frac{1}{152}$ its weight of antimony, the compound was perfectly brittle; and even the fumes of antimony in the vicinity of melted gold are sufficient to destroy its ductility. (Hatchett, *Phil. Trans.*, 1803.) With potassium and sodium it forms white brittle compounds, destructible by the action of air and water.

The *alloy of potassium and antimony* may be formed by heating to redness in a covered crucible a mixture of equal parts of finely-powdered antimony and tartar for about three hours. When cold, the crucible must be broken, the button of alloy freed from the scoriæ, broken into pieces, and preserved in a well-stopped phial. By substituting tartrate of soda for common tartar, the *alloy of sodium and antimony* may be obtained; and a mixture of soda-tartrate of potassa and powdered antimony yields the *triple alloy of antimony, potassium, and sodium*. When these alloys are reduced to powder, and exposed to the air, they heat, and take fire like pyrophorus.

Its alloys with manganese and with zinc have not been examined.

Alloyed with lead in the proportion of 1 to 16, and a small addition of copper, antimony forms the alloy used for *printers' types*. With lead only, a white and rather brittle compound is formed, used for the plates upon which music is engraved. With iron it forms a hard whitish alloy formerly called *martial regulus*, which may be obtained by fusing two parts of sulphuret of antimony with one of iron filings; a scoria consisting chiefly of sulphuret of iron is formed, and the fused alloy beneath usually presents a stellated appearance in consequence of its crystallization. This star was much admired by the alchemists, who considered it a mysterious guide to transmutation. With tin, antimony constitutes a kind of *pewter*, a term, however, which has also been applied to some other alloys, especially that of lead and tin. The finest pewter consists of about 12 parts of tin and 1 of antimony, with a small addition of copper. A good white metal, used for tea-

pots, is composed of 100 tin, 8 antimony, 2 bismuth, and 2 copper.

The analysis of an alloy of tin, lead, copper, and antimony, may be thus performed:—Introduce 100 grains in powder into a matrass with a wide mouth, and pour upon it 1 ounce of water and 2 of nitric acid; digest and evaporate to dryness. The dry mass will consist of the nitrates of lead and copper, which are soluble, and may be taken up by two ounces of hot water, and of the peroxides of tin and antimony, which are insoluble, and remain upon the filter.

To the solution of the nitrates add sulphate of soda, which throws down sulphate of lead, and which is to be collected in a filter, washed, dried at a red heat, and weighed. The filtered liquor may be evaporated to about two ounces in bulk, and having rendered it slightly acid by dilute sulphuric acid, immerse in it a plate of iron, which will throw down metallic copper, to be purified if requisite, dried, and weighed.

The separation of the peroxides of tin and antimony is attended with many difficulties: it may be imperfectly effected by solution in nitromuriatic acid, and subsequent dilution with a large quantity of water, which throws down the antimonial oxide, not however pure, but with a portion of peroxide of tin: the latter, retaining a little peroxide of antimony, may be procured by evaporation and exposure of the residue to a dull red heat in a porcelain cup.

Section XVI. BISMUTH.

THIS metal is found native, combined with oxygen, and with arsenic and sulphur.

Native Bismuth occurs crystallized in octoëdra and cubes, and generally contains arsenic and sometimes cobalt. It has been found in Cornwall, and in Germany, France, and Sweden.

The metal may be obtained pure, by dissolving the bismuth of commerce in nitric acid; water is added to the nitric solution, which separates subnitrate of bismuth. This compound is easily reduced in the usual way with a little black flux at a moderate heat.

Bismuth is a brittle white metal, with a slight tint of red : its specific gravity is 9.822. (Hatchett, *Phil. Trans.* 1803.) It fuses at 476° , and always crystallizes on cooling. According to Chaudet, pure bismuth is somewhat flexible. A cast bar of the metal, $\frac{1}{10}$ th of an inch diameter, supports, according to Muschenbrock, a weight of forty-eight pounds. Bismuth is volatile at a high heat, and may be distilled in close vessels.

Bismuth and Oxygen.—When bismuth is exposed to heat and air it oxidizes, forming a fusible *white oxide*. If the heat be increased by directing a current of oxygen upon the metal, it burns with much brilliancy, and produces an abundant yellow smoke, which condenses in the form of a yellowish white sublimate. The readiest mode of obtaining oxide of bismuth, consists in dissolving bismuth in nitric acid, precipitating by dilution with water, edulecorating the precipitate, and heating it, when dry, to dull redness. When in fusion this oxide acts upon other oxides much in the same way as oxide of lead. It forms, on cooling, a vitreous mass of a specific gravity of 8.2.

The equivalent of bismuth, deduced from the experiments of J. Davy on the chloride, and of Langerhielm on the oxide, is 72, and the oxide consists of

1 proportional of bismuth	.	.	.	=	72
1 " oxygen	.	.	.	=	8
					<hr/>
Equivalent of oxide of bismuth	.	.	.	=	80

Oxide of bismuth occurs, though very rarely, *native* : it has been found in Cornwall and Saxony.

Chloride of Bismuth is procured by gently heating the metal in the gas ; it burns with a blue flame, and forms a gray compound. This chloride may also be prepared by heating two parts of corrosive sublimate with one of powdered bismuth, and expelling the excess of the former and the mercury by heat. It was formerly called *Butter of Bismuth*. It is of a gray colour, and fuses at about 480° . In close vessels it does not sublime at a red heat. When exposed to air it deliquesces. It consists of

1 proportional of bismuth	.	.	.	=	72
1 " chlorine	.	.	.	=	36
					<hr/>
Equivalent of chloride of bismuth	.	.	.	=	108

Chlorate of Bismuth has not been examined.

Iodide of Bismuth, obtained by heating iodine with the metal, is of an orange-colour, and insoluble in water. When hydriodic acid or hydriodate of potassa is added to nitrate of bismuth, a precipitate falls of a deep chocolate-brown colour insoluble in water, but soluble in liquid potassa.

Iodate of Bismuth is thrown down upon adding iodate of potassa to nitrate of bismuth. It is white and insoluble.

The action of *bromine* and *bromic acid* upon bismuth has not been examined.

Fluoride of Bismuth is a soluble compound.

Nitrate of Bismuth.—This salt is made by dissolving the metal to saturation in two parts of nitric acid and one of water : the action is rapid, and nitric oxide is copiously evolved. The solution affords four-sided prismatic crystals, which are decomposed at a red heat, and leave oxide of bismuth. They contain

1 proportional of oxide of bismuth	.	.	.	=	80
1 ,, nitric acid	.	.	.	=	54
					<hr/>
Equivalent of nitrate of bismuth	.	.	.	=	134

and probably three proportionals of water. Ammonia occasions a precipitate in nitrate of bismuth, which is re-dissolved by excess of the alkali. Potassa and soda also throw down the oxide, which is but sparingly soluble in those alkalis. Nitrate of bismuth is decomposed by water, and a fine white powder, called *magistery of bismuth*, *pearl white*, or *blanc de fard*, is precipitated, which is a hydrated subnitrate of bismuth. In this state it has been used in medicine as a tonic.—*Quarterly Journal*, viii. 295. If characters be written on paper with nitrate of bismuth they are invisible when dry, but become white and legible on immersion in water, thus forming a *white sympathetic ink*. The same characters are rendered brown or black by solution of sulphuretted hydrogen. It is sometimes stated, that the salts of bismuth are blackened by exposure to light, but such an effect depends upon their containing a minute portion of silver.

Sulphuret of Bismuth is of a bluish colour and metallic lustre ; it consists of

1 proportional of bismuth	=	72
1 ,, sulphur	=	16
					<hr/>	
Equivalent of sulphuret of bismuth	=	88

The compound analyzed by Vauquelin appears to have been a *bisulphuret*.—*Annales du Museum*, tom. xv.

Native Sulphuret of Bismuth has been found in Cornwall, Bohemia, Saxony, and Sweden. It occurs massive and acicular, its lustre is metallic, and its colour bluish gray. It is a very rare mineral.

Hyposulphite of Bismuth has not been examined.

Sulphite of Bismuth is an insoluble white powder, which is not taken up by excess of the acid.

Sulphate of Bismuth is obtained by dissolving the oxide in sulphuric acid and evaporating to dryness. It is a white compound, insoluble in, but decomposed by, water, which converts it into a *subsulphate* and *supersulphate*.

Hydrosulphuretted Oxide of Bismuth is of a deep brown approaching to black. It is thrown down from nitrate of bismuth by sulphuretted hydrogen.

Phosphuret of Bismuth does not, according to Pelletier, exist; at least, it cannot be formed by the usual process of projecting phosphorus upon the hot metal. When phosphuretted hydrogen gas is passed into nitrate of bismuth, a dark brown precipitate ensues, which, when collected and dried, has the properties of a true phosphuret of the metal.

Neither the *hypophosphite*, nor *phosphite*, have been examined.

Phosphate of Bismuth is formed, according to Wenzel, by digesting the oxide in phosphoric acid; an insoluble subphosphate, and a soluble and crystallizable phosphate, are the results.

Carbonate of Bismuth is thrown down from the nitrate by carbonated alkalis: it is a white powder, insoluble in carbonic acid.

Ferrocyanate of Bismuth has not been examined.

Borate of Bismuth is a white powder, insoluble in water.

Alloys of Bismuth.—Bismuth forms alloys, some of which are remarkable for their fusibility. With gold, platinum, and silver, it forms brittle compounds. A compound of eight parts of bismuth, five of lead, and three of tin, liquefies at 212° ; it is called Sir I. Newton's *fusible metal*. The addition of one part of quicksilver renders it yet more fusible. Bismuth enters into the composition of *soft solders*. These alloys are mostly white, brittle, and easily oxidated. Combinations of bismuth with potassium and sodium may be obtained by the same process as the corresponding alloys of antimony.

Section XVII. COBALT.

THE native combinations of cobalt are the oxide, and compounds of the metal with iron, nickel, arsenic, and sulphur. It is also found combined with arsenic acid. In the white and gray cobalt ores, the metal is combined with iron, and with arsenic: some of the varieties are crystallized in cubes, octoëdrons, and dodecaëdrons. The red ore is an arseniate. The finest specimens are the produce of Saxony. Cobalt has also been detected, by Stromeyer, in several specimens of metallic iron.

Cobalt is never employed in the metallic state, so that the processes for its reduction are generally carried on upon a small scale, and confined to the experimental laboratory.

To obtain pure cobalt, the cobalt of commerce, in fine powder, may be calcined with four parts of nitre, and washed in hot water, by which arsenic is separated: then digest in dilute nitric acid, and immerse a plate of iron, which will separate the copper; filter and evaporate to dryness; digest the dry mass in liquid ammonia and filter; expel the excess of ammonia from the filtered liquor by heat, taking care not to produce a precipitate, and then add solution of potassa, which throws down oxide of nickel; filter immediately, and boil, which will occasion the separation of oxide of cobalt, and which, ignited with charcoal, furnishes the pure metal. In this process the first calcination with nitre often requires two or three repetitions in order to get rid of the whole of the arsenic, which adheres to cobalt with much obstinacy.

When the ores of cobalt are dissolved in muriatic acid by the aid of a little nitric acid, and sulphuretted hydrogen passed through the solution, the arsenic is precipitated: the filtered liquor may then be boiled with a little nitric acid to peroxidize the iron, and precipitated by carbonate of potassa: the precipitate, when well washed, is to be digested in oxalic acid, which leaves an insoluble oxalate of cobalt: this may be decomposed at a high heat. When dry hydrogen gas is passed over oxide of cobalt, it is also reduced.

Cobalt is of a reddish gray colour, brittle, and difficultly

fusible. Its specific gravity, according to Bergman and others, is 7.7. Tassaert and Lampadius place it at 8.5 and 8.7. It is magnetic.

Cobalt and Oxygen unite in two proportions. *Protoxide of Cobalt* is formed by adding potassa to the nitrate, and washing and drying the precipitate; it appears very dark blue or nearly black. By exposure to heat and air it absorbs an additional portion of oxygen, and is thus converted into black *peroxide*. The protoxide, when recently precipitated and moist, is *blue*; and, if left in contact of water, becomes a *red hydrate*. The composition of the protoxide of cobalt, deduced from the analysis of the chloride, is 100 cobalt + 24.7 oxygen; and this result nearly agrees with those published by Proust, (*Annales de Chimie*, vol. lx.) and Rothoff, (*Ann. of Phil.* vol. iii.) It appears, from the experiments of the latter chemist, that the peroxide of cobalt contains 100 metal + 36.7 oxygen, which, in reference to the above deduction from the chloride, would lead us to consider it as containing one proportional of cobalt and one and a half of oxygen. All the salts of cobalt contain the protoxide. The number 30 may probably be assumed, without material error, as the equivalent of cobalt, and the oxides contain

1 proportional of cobalt	=	30
1 " oxygen	=	8
						<hr/>
Equivalent of protoxide of cobalt	=	38
1 proportional of cobalt	=	30
1½ " oxygen	=	12
						<hr/>
Equivalent of the peroxide	=	12

Acted upon by muriatic acid the peroxide of cobalt evolves chlorine, and affords a solution of the protoxide. When heated in close vessels it loses oxygen and becomes protoxide.

Cobalt and Chlorine.—Cobalt burns when heated in chlorine, and forms *chloride of cobalt*. When muriate of cobalt is evaporated to dryness, and the residuum heated to redness out of the contact of air, a substance of a blue colour and micaceous texture is obtained, which is a pure chloride of cobalt. It dissolves perfectly in water, forming a pink solution. As the chloride of cobalt is easily formed, and appears to be a perfectly definite compound, it offers an unexceptionable sub-

stance, from which, by analysis, to deduce the equivalent number of the metal. For this purpose 32 grains of the pure chloride were dissolved in water, and decomposed by solution of nitrate of silver: the precipitate of chloride of silver, dried at a dull red heat, weighed 68 grains, which is the equivalent of 16.73 grains of chlorine; hence the 32 grains of chloride of cobalt are composed of 16.73 chlorine + 15.27 cobalt; and $16.73 : 15.27 :: 36 : 32$, = the equivalent of cobalt, a number somewhat higher than that above assumed upon the authority of Rothoff. The chloride of cobalt, therefore, may be considered as composed of

1 proportional of cobalt	= 30
1 „ chlorine	= 36
Equivalent of chloride of cobalt					<hr/> = 66

The hydrated chloride, usually called *Muriate of Cobalt* is a deliquescent salt, of a blue-green colour; it may be formed by digesting either oxide in muriatic acid; if the peroxide be used, chlorine is evolved, and it passes to the state of protoxide. When a little diluted, this solution becomes pink; the pale pink solution, when written with, is scarcely visible; but if gently heated, the writing appears in brilliant green, which soon vanishes as the paper cools, in consequence of the salt absorbing the ærial moisture. This solution has been termed *Hellot's sympathetic ink*. By careful evaporation, muriate of cobalt forms red rhombic crystals, composed of one proportional of the chloride and five of water.

Iodide and Iodate of Cobalt remain unexamined. No precipitate is produced in muriate of cobalt either by hydriodic acid or hydriodate of potassa.

Nothing is known of the action of bromine upon cobalt.

Fluoride of Cobalt.—When oxide of cobalt is digested in hydrofluoric acid, a pink solution is obtained, which yields crystals on evaporation, difficultly soluble in water.

Nitrate of Cobalt.—With nitric acid the oxide of cobalt furnishes a red deliquescent salt in irregular rhombic crystals, consisting, according to Dr. Thomson, of

1 proportional of protoxide of cobalt	= 38
1 „ nitric acid	= 54
6 proportionals of water (9 × 6)	= 54
					<hr/> 146

Ammoniuret of Cobalt.—Ammonia digested upon recently precipitated protoxide of cobalt, slowly dissolves it, and forms a pale pink solution, which becomes deeper coloured by exposure to air, in consequence, it is said, of the metal passing to the state of peroxide. The ammoniacal solution of the peroxide forms acicular crystals of a beautiful pink colour.

Sulphuret of Cobalt is formed by heating the oxide with sulphur. It is yellowish-white.

Neither the *Sulphite* nor the *Hyposulphite of Cobalt* have been examined.

Hyposulphate of Cobalt forms, according to Heeren, a red saline mass, very soluble, but not deliquescent.

Sulphate of Cobalt forms red rhombic crystals, soluble in 24 parts of water at 60°, and insoluble in alcohol. It may be made by dissolving the newly precipitated protoxide in sulphuric acid diluted with its bulk of water. In its crystallized state it consists of

1 proportional of protoxide of cobalt	.	.	.	=	38
1 „ sulphuric acid	.	.	.	=	40
7 proportionals of water (9 × 7)	.	.	.	=	63
					<hr/>
					141

When dried at a temperature of 500°, the crystals fall into a blue powder, which, in a bright red heat, fuses, and gives out sulphuric acid, leaving a black oxide. The blue powder is the *anhydrous sulphate of cobalt*, perfectly soluble in water, and forming a pink solution; it is slightly deliquescent, and becomes lilac-coloured by exposure to air.

Fifty grains of dry sulphate of cobalt dissolved in water, furnished a precipitate with muriate of baryta, amounting, when dried at a red heat, to 75 grains of sulphate of baryta, which is the equivalent of 25.5 grains of sulphuric acid: this method of analysis, therefore, shows that sulphate of cobalt consists very nearly of equal weights of sulphuric acid and protoxide of cobalt, and may be considered as verifying the above statements.

Bisulphate of Cobalt is formed by digesting the sulphate in excess of acid; the solution affords prismatic efflorescent crystals, composed of

1 proportional protoxide of cobalt	
2 proportionals sulphuric acid	
3 „ water.	

Ammonio-sulphate and *Potassa-sulphate of Cobalt*.—Sulphate of cobalt forms triple compounds with potassa and with ammonia, which have not been minutely examined. If it contain nickel, the crystals are of a greenish tinge, but pink when the cobalt is pure.

Hydrosulphuretted Oxide of Cobalt is precipitated from the muriate by hydrosulphuret of ammonia, of a black colour. Sulphuretted hydrogen does not throw down cobalt from solutions with excess of acid; but it occasions precipitates in those which are perfectly neutral.

Phosphuret of Cobalt is a white brittle compound.

Hypophosphite of Cobalt forms, according to Rose, octoëdral efflorescent crystals containing 49.35 *per cent.* of water of crystallization.

Nothing is known respecting the *Phosphite of Cobalt*.

Phosphate of Cobalt may be formed by double decomposition, as by adding phosphate of soda to muriate of cobalt; it is insoluble in water of a lilac colour; and soluble in excess of phosphoric acid; if mixed with two or three parts of pure alumina, and exposed in a covered crucible to a full white heat, it produces a beautiful blue colour, which may sometimes be employed by painters as a substitute for ultramarine. (THENARD.) The theoretical composition of anhydrous phosphate of cobalt is,

1 proportional of protoxide of cobalt	.	.	.	=	38
1 ,, phosphoric acid	.	.	.	=	28
					<hr/>
					66

Carbonate of Cobalt is formed by decomposing the nitrate, muriate, or sulphate of cobalt by carbonate of potassa, or soda; a reddish blue powder is precipitated, becoming pink when dried, and readily soluble with effervescence in the acids. It consists, when carefully dried, of

1 proportional of protoxide of cobalt	.	.	.	=	38
1 ,, carbonic acid	.	.	.	=	22
					<hr/>
					60

Heated in close vessels it gives off carbonic acid, and a gray protoxide of cobalt remains. It dissolves in excess of carbonic acid.

Ammonio-carbonate of Cobalt.—Carbonate of cobalt is readily soluble in solution of carbonate of ammonia, forming a bright pink liquid.

Ferrocyanate of Potassa forms a grass-green precipitate in solutions of cobalt.

Solution of borax produces a pink precipitate in solution of muriate of cobalt, which is a *borate of cobalt*, and which produces a beautiful blue glass when fused.

The *salts of cobalt* all contain the protoxide; they are decomposed by ammonia, which, if added in excess, re-dissolves the oxide: phosphoric, carbonic, arsenic, and oxalic acids, produce, by double decomposition, insoluble red or lilac precipitates in these solutions.

The *alloys of cobalt* are unimportant.

The chief use of cobalt is in the state of oxide as a colouring material for porcelain, earthenware, and glass: it is principally imported from Germany in the state of *zaffre*, and *smalt* or *azure*.

Zaffre is prepared by calcining the ores of cobalt, by which sulphur and arsenic are volatilized, and an impure oxide of cobalt remains, which is mixed with about twice its weight of finely-powdered flints.

Smalt and *azure blue* are made by fusing *zaffre* with glass; or by calcining a mixture of equal parts of roasted cobalt ore, common potash, and ground flints. In this way a blue glass is formed, which, while hot, is dropped into water, and afterwards reduced to a very fine powder.

Section XVIII. URANIUM.

THE *native hydrated oxide* of this metal has been termed *Uranite*, or *Uranitic Mica*. Its crystalline form is the cube, and several modifications; it often occurs in thin quadrangular plates. It exhibits various shades of yellow and green. It has been found in France; and of great beauty near Callington, in Cornwall.

The *ferriferous oxide of uranium* was formerly mistaken for an ore of zinc, and called *Pechblende*, till Klaproth, in 1789, demonstrated it to contain uranium. It is a compound of protoxide of uranium and iron, with lead, copper, and other substances. From this ore uranium may be obtained by the following process: Reduce it to powder, and expose it to heat in a muffle; then digest in nitric acid, diluted with four parts of water, taking care to employ excess of the mineral, by which the solution of the iron is nearly prevented. The nitric solution is filtered, and sulphuretted hydrogen passed through it to throw down lead and copper; the clear solution being poured off, is boiled, filtered, and evaporated, and crystals of nitrate of uranium are deposited.

Uranium was obtained by Arfwedson, by passing hydrogen over the protoxide, heated in a glass tube. It was crystalline, of a metallic lustre, is of a gray-brown colour, brittle, and very difficult of fusion; its specific gravity has not been ascertained with precision. Bucholz states it as = 9.0.—Gehlen's *Journal*, iv.

Hitherto few experiments have been made upon this metal. It appears susceptible of two degrees of oxydizement.

Protoxide of Uranium is obtained by strongly heating the pernitrates: it is of a dark green colour; it is very feebly acted on by the greater number of the acids; and the solutions and salts are green: nitric acid converts it into peroxide. It is soluble in ammonia.

Peroxide of Uranium.—When a solution of pernitrates of uranium is precipitated by caustic potassa, a yellow powder falls, which was regarded as a pure hydrated peroxide,

but it always retains potassa; and if other precipitants are employed, they also are in part carried down by it; so that the peroxide cannot thus be obtained pure. As thrown down by potassa, it is soluble in the carbonated alkalis, with which it forms triple salts; and we are thus enabled to separate uranium from iron. Peroxide of uranium is not precipitated by sulphuretted hydrogen; a strong heat decomposes it, and converts it into protoxide: it is sometimes used to produce a deep yellow upon porcelain.

The statements of different chemists respecting the composition of these oxides are much at variance. According to Thomson, the equivalent of uranium is 200², that of the protoxide 216, and of the peroxide 224; but Berzelius and Arfwedson (*Ann. of Phil.*, N.S. ii.) state that the oxygen in the protoxide is to that in the peroxide as 1 to 1.5, and their equivalent of the metal is 216.

Chloride of Uranium.—When the muriatic solution of the peroxide of uranium is evaporated to dryness, and heated in a small retort, it loses water, and a yellow-green chloride remains, which is readily soluble in water, alcohol, and ether. The ethereal solution exposed to light becomes dirty-green and turbid.

Potassa-chloride of Uranium crystallizes from its concentrated solution, and forms a triple salt, soluble in alcohol.

The action of iodine, bromine, and fluorine upon uranium has not been examined.

Nitrate of Uranium, formed as above directed, yields yellow prismatic and tabular crystals, very soluble, and somewhat deliquescent in a moist air. They are also readily soluble in alcohol and ether, and when the latter solution is exposed to light, it is decomposed, becomes green, and deposits the protoxide.

Subnitrate of Uranium, upon the authority of Bucholz, is formed by heating the nitrate, which renders a part insoluble in water, and separates in the form of a yellow powder.

Sulphuret of Uranium was obtained by Rose, by passing the vapour of sulphuret of carbon over the protoxide, at a high heat. The alkaline hydrosulphurets form black precipitates in the pure solutions of uranium.

Protosulphate of Uranium forms green prismatic crystals:

it may be formed by boiling the protoxide in sulphuric acid. With sulphate of potassa it produces a triple salt.

Persulphate of Uranium forms yellow prismatic crystals, decomposable by heat, and, according to the analysis of Bucholz, consisting of 70 oxide, 18 acid, 12 water, = 100.

Its alcoholic solution becomes ethereal and green when exposed to the sun's rays, and deposits a precipitate, which is a subsulphate of the protoxide.

Potassa-persulphate of Uranium forms yellow crystals, soluble in alcohol.

Phosphuret of Uranium has not been examined.

Perphosphate of Uranium is a difficultly soluble yellow salt: it is soluble in excess of phosphoric acid. It exists native in the micaceous ore of uranium.

Percarbonate of Uranium is precipitated by a carbonated alkali from the solutions of the peroxide, but it loses carbonic acid on drying.

Ferrocyanate of Uranium is thrown down in the form of a rich brown, and very characteristic precipitate: in colour it much resembles the ferrocyanate of copper.

The protosalts of uranium have a green and the persalts a yellow colour, and an astringent metallic taste. Potassa forms in the solutions of the latter a yellow precipitate, and carbonate of potassa a straw-coloured precipitate: both these precipitates are insoluble in excess of pure alkali, but dissolve in the alkaline carbonates. Ferrocyanate of potassa and tincture of galls produce brown precipitates in solutions of uranium. The salts are mostly soluble in alcohol and in ether, and acquire a green colour by exposure to the sun's rays. The protosalts have been very little examined.

Section XIX. TITANIUM.

TITANIUM was first recognised as a distinct substance by Mr. Gregor, and some of its compounds were afterwards examined by Klaproth. For our knowledge of the properties of *Titanium* in its metallic state we are chiefly indebted to Dr. Wollaston, who discovered it in small cubic crystals, having the lustre of burnished copper, in the slag of the iron furnaces at Merthyr Tydvil, in South Wales (*Phil. Trans.* 1823, p. 17). These crystals are titanium, almost absolutely pure: they have the following properties:—They are so hard as to scratch rock crystal; they are not acted on by nitric, muriatic, or sulphuric acids, nor are they soluble in nitro-muriatic acid. Before the blowpipe they are infusible; they are, however, superficially oxidated by a continued heat, becoming of a purple or red colour. Borax has no action on them, but only removes the superficial oxide. Nitre oxidates them on the surface. The combined action of nitre and borax soon effects their solution; but as these salts do not unite by fusion, the addition of soda accelerates their action. The fused mass becomes opaque on cooling by the deposit of a white oxide, which may either be previously freed of the salts by boiling water, and then dissolved in muriatic acid, or the whole mass may be at once dissolved together. In either case, alkalis precipitate from the solution a white oxide, insoluble in excess of alkali, either pure or carbonated. By evaporating the muriatic solution to dryness at 212°, it is freed of redundant acid, and a soluble muriate remains, in a favourable state for exhibiting the characteristic properties of the metal.

Titanium exists in the state of oxide in the minerals called *titanite* and *menuchanite*. *Titanite* is a nearly pure oxide of titanium; it is of a brown colour, and occurs embedded in the quartz and granite of primitive countries, and sometimes traverses rock crystals in fine hair-like filaments. In this country it occurs at Bedgellert, in Caernarvonshire; and near Killin, in Scotland. The finest specimens are those from the vicinity of Mont Blanc and St. Gothard. The mineral, known by the

name of *anatase*, *octoëdrite*, and *oysanite*, is nearly of the same nature as titanite. It is found in Bavaria, Norway, Switzerland, and in the valley of Oysans in France. *Menachanite* consists principally of oxides of titanium and iron; it is found in the bed of a small stream at Menachan, in Cornwall. *Nigrine*, *iserine*, *rutilite*, and *sphene*, are also ores of titanium.

According to Laugier (*Ann. de Chim.* lxxxix. 306) the metal may be obtained from titanite by fusion with potassa; the fused mass, washed with water, leaves oxide of titanium, containing a little iron; it is to be dissolved in muriatic acid, and precipitated by oxalic acid. The oxalate affords the metal by intense ignition with charcoal: it is, however, not possible to obtain it in any state of agglutination.

From menachanite, white oxide of titanium may be obtained by fusing it with potassa, and adding muriatic acid to the alkaline solution, so as merely to neutralize the alkali and precipitate the oxide; to separate a little adhering iron, this must be dissolved in excess of muriatic acid, and precipitated by oxalic acid as before.

Oxides of Titanium.—Titanium is said to be susceptible of two, or, according to some chemists, of three degrees of oxydizement. The mineral called *anatase*, is regarded as the *protoxide*, but its properties and composition have not been determined, and it is the peroxide only which has been particularly examined.

Peroxide of Titanium may be obtained from rutilite, by fusing it in fine powder, in a platinum crucible, with thrice its weight of pure carbonate of potassa: a gray mass is obtained, which, after having been washed with water, is dissolved in muriatic acid, and on diluting with water, and boiling the solution, the greater part of the oxide of titanium is precipitated; it is collected, and washed with very dilute muriatic acid. In this state it still is apt to retain traces of iron and manganese, which may be separated by digesting the moist precipitate with hydrosulphuret of ammonia, which forms sulphurets with the iron and manganese, but does not affect the oxide of titanium. Dilute muriatic acid removes the sulphurets; and the oxide of titanium, after being again washed and heated red-hot, is pure. (Rose, *Ann. de Chim et de Phys.* xxiii.)

This oxide of titanium is white, infusible, and difficult of reduction : when recently precipitated it dissolves in some of the acids, but becomes nearly insoluble after it has been ignited. Its solution in muriatic acid is always very sour, and part of the oxide falls down when it is heated to the boiling point, but by careful evaporation to dryness, a soluble muriate remains. It is precipitated by the pure and carbonated alkalis ; infusion of galls, and ferrocyanate of potassa throw it down of a characteristic red colour. When a rod of zinc is immersed in the muriatic solution of peroxide of titanium, a purple precipitate, probably of the protoxide, is obtained ; but it soon acquires oxygen, and becomes white. The recently precipitated peroxide is with difficulty separated from water upon a filter, but passes through in a milky state ; the addition of a little acid or alkali facilitates its separation. It seems doubtful whether this oxide forms any definite salts with the salts : it unites with the alkalis, and has thence been termed *titanic acid*. From the experiments of Rose and Thomson, it appears that 32 is the equivalent of titanium ; and the peroxide consists of

1	proportional of titanium	.	.	.	= 32
2	„ oxygen (8 × 2)	.	.	.	= 16
					<hr/> 48

The *blue* oxide is formed by exposing the metal to heat and air ; the *red* is the native oxide ; and the *white* is that which is precipitated from the alkaline solution of titanite and menachanite by muriatic acid. According to Vauquelin and Hecht (*Journal des Mines*, No. xv.), the white oxide contains 89 parts of red oxide and 11 of oxygen.

Chloride of Titanium was obtained by Mr. George (*Annals of Phil.*, N. S., ix. 18) by passing dry chlorine over metallic titanium, heated to redness. It is a dense, transparent, and colourless fluid, fuming when exposed to air. It boils at a little above 212°, and acts violently upon water, evolving chlorine, and furnishing, when the water is not in excess, a white salt, very soluble, and deliquescent, having the properties of muriate of titanium. It would appear, therefore, that the original liquid is a bichloride of titanium, which evolves chlorine, becoming a protochloride, and ultimately a proto-muriate, by the action of water. Mr. George's experiments

render it probable that the perchloride contains one proportional of metal and four of chlorine, and that the protochloride consists of one proportional of titanium and two of chlorine.

Fluoride of Titanium.—The peroxide of titanium readily dissolves in hydrofluoric acid.

Sulphuret of Titanium was obtained by M. Rose, by passing the vapour of sulphuret of carbon over peroxide of titanium. It has a dark green colour and metallic lustre. (*Quarterly Journal*, xvi. 97.)

Phosphuret of Titanium is formed, according to Chenevix, by heating the phosphate with charcoal; it has a white metallic lustre, and is brittle.

Section XX. CERIUM.

THIS metal was obtained by Hisinger and Berzelius, from a mineral found at Bastnas in Sweden, to which they have given the name of *cerite*. It is also contained in *Allanite*, a mineral from Greenland, first distinguished as a peculiar species by Mr. Thomas Allan, of Edinburgh. It contains, according to Dr. Thomson's analysis, about 40 *per cent.* of oxide of cerium.

The ore is calcined, pulverized, and digested in nitro-muriatic acid. To the filtered solution, from which part of the excess of acid has been boiled off, oxalic acid is added, which occasions a white precipitate: this, when dried and ignited, is peroxide of cerium.

This oxide is extremely difficult of reduction. Mr. Children succeeded in fusing it by the aid of his powerful Voltaic apparatus, and when intensely heated it burned with a vivid flame, and was partly volatilized. Vauquelin describes cerium as a hard white brittle metal.—*Annales de Chimie*, vol. iv.

Vauquelin and Hisinger have described two *oxides of cerium*. The *protoxide* is white, and may be obtained by precipitation from its muriate: it forms salts with the acids, from which the alkalis throw down a white hydrate; the carbonated alkalis a white carbonate, soluble in excess of the precipitant; and oxalate of ammonia a white oxalate.

The *Peroxide of Cerium* is formed by exposing the protoxide to the joint action of heat and air: it is of a reddish colour, and is dissolved by several of the acids. Digested in muriatic acid it yields a solution of the protoxide, with the disengagement of chlorine.

The equivalent of cerium appears to be about 50. The protoxide consisting of

1 proportional of cerium	= 50
1 " oxygen	= 8
					<hr/>
					58

And the peroxide of

1 proportional of cerium	= 50
1½ " oxygen	= 12
					<hr/>
					62

Chloride of Cerium.—When the solution of the protoxide in muriatic acid is evaporated to dryness, a white deliquescent *protochloride* is obtained, which is readily soluble in water and in alcohol. The peroxide of cerium also dissolves in muriatic acid, furnishing a brown solution: when it is gently heated chlorine is evolved, and a protochloride formed.

Fluoride of Cerium is an insoluble yellow powder: it has been found native in the mines of Fahlun in Sweden.

Sulphuret of Cerium may be obtained, according to Mosander, by passing the vapour of sulphuret of carbon over red-hot carbonate of cerium; or by fusing oxide of cerium with excess of sulphuret of potassium, and removing the soluble parts by washing with water. It is a yellow compound, and appears to consist of

1 proportional of cerium	= 50
1 " sulphur	= 16
					<hr/>
					66

Protosulphate of Cerium may be obtained by digesting the protocarbonate in dilute sulphuric acid: it yields small crystals, of a purplish tint, and difficultly soluble in water.

Persulphate of Cerium is a lemon-yellow salt, from which a red heat expels half the acid, and converts it into a red *subpersulphate*.

Phosphuret of Cerium is precipitated upon a stick of phosphorus immersed in a solution of the chloride.

Protophosphate of Cerium is an insoluble white powder, soluble in muriatic and nitric acids, but insoluble in excess of phosphoric acid.

Carburet of Cerium is obtained, according to Mosander, by heating the oxalate in a retort.

Protocarbonate of Cerium is precipitated by the carbonated alkalis, in the form of a white insoluble powder. It is decomposed by heat. It has been found native.

Percarbonate of Cerium much resembles the protocarbonate in appearance, but it is heavier, and of a less pure white colour.

The protosalts of cerium are colourless, or slightly purple, of a sweet and astringent taste, and bear much general resemblance to the salts of yttrium. They are unaltered by sulphuretted hydrogen, but are precipitated by the hydrosulphuretted alkalis. Ferrocyanate of potassa occasions in them a white precipitate. The salts of the peroxide are of a yellow colour, and the hydrosulphurets occasion in them a white precipitate.

Section XXI. TELLURIUM.

THE ores of tellurium are, 1. *Native*, in which the metal is combined with iron and a little gold. 2. *Graphic ore*, which consists of tellurium, gold, and silver. 3. *Yellow ore*, a compound of tellurium, gold, lead, and silver; and 4. *Black ore*, consisting of the same metals with copper and sulphur.

These ores have only been found in the Transylvanian mines, and in Siberia.

The metal is extracted from them by precipitating their diluted nitro-muriatic solution by potassa, which is added in excess: the clear liquor is poured off, and saturated with muriatic acid, which affords a precipitate of oxide of tellurium. This, heated in a glass retort with charcoal, furnishes the metal. Tellurium is of a bright gray colour, brittle, easily fusible, and very volatile. Its specific gravity is 6.1.

Oxide of Tellurium.—Exposed to heat and air, tellurium readily burns, exhaling a peculiar odour, which Berzelius ascribes to selenium, and forming a yellowish white oxide, con-

sisting, according to Klaproth (*Beiträge*, vol. iii.) of tellurium 100—oxygen 20.5. The more recent experiments of Berzelius, however, give 32 as the equivalent of tellurium; and the oxide consists of

1	proportional of tellurium	=	32
1	„ oxygen	=	8
							<hr/>
							40

Oxide of tellurium is also obtained by evaporating the nitrate to dryness, and exposing the residue to a dull red heat. If it be precipitated from its solutions by alkalis, it generally retains a portion of the precipitant.

Chloride of Tellurium is a white fusible compound, formed by heating the metal in chlorine. According to Davy (*Elements*, p. 410), it consists of 2 tellurium + 1.85 chlorine; but as his experiments were made upon a very limited quantity of materials, it is probable that it contains

1	proportional of tellurium	=	32
1	„ chlorine	=	36
							<hr/>
							68

The solution of oxide of tellurium in muriatic acid is precipitated as a subsalt by water; excess of water redissolves it.

The *Chlorate of Tellurium* is not known.

Iodide of Tellurium.—Iodine readily combines with tellurium, forming a deep brown compound, which dissolves in water, forming the *hydriodate of tellurium*. The *Iodate of Tellurium* has not been examined.

Tellurium and Hydrogen unite in two proportions: when tellurium is negatively electrized in contact with water, a brown powder is produced, which is the solid *hydruret*: when an alloy of tellurium and tin is acted on by muriatic acid, *telluretted hydrogen gas* is evolved; it reddens litmus, dissolves in water, and possesses the general habitudes of sulphuretted hydrogen; it consists, according to Berzelius, of

1	proportional of tellurium	=	32
1	„ hydrogen	=	1
							<hr/>
							33

in which case, 100 cubical inches must weigh 69.895 grains:

its specific gravity, compared with hydrogen, being 33, and with common air 2.91.

The salts of tellurium are decomposed by the alkalis, and the precipitate is redissolved when they are added in excess. Hydrosulphuret of ammonia forms a brown precipitate; ferrocyanate of potassa occasions no change. Zinc or iron, immersed into the solutions, cause the separation of metallic tellurium.

The oxide of tellurium combines with many of the metallic oxides, acting the part of an acid, and producing a class of compounds which have been called *tellurates*.

Tellurate of Potassa may be formed by heating oxide of tellurium with nitre, and dissolving the residuum in boiling water, which, on cooling, deposits an imperfectly crystallized white powder, difficultly soluble in water.

Solution of tellurate of potassa added to solutions of lime, baryta, strontia, copper, and lead, forms insoluble tellurates of the oxides of those metals.

Section XXII. ARSENIC.

THIS metal may be obtained from the white arsenic of commerce, by mixing it with its weight of black flux*, and introducing the mixture into a Florence flask or small retort, placed in a sand bath, gradually raised to a red heat: a brilliant metallic sublimate of pure arsenic collects in the upper part of the flask or in the neck of the retort. The volatility of white arsenic prevents its easy reduction by charcoal alone; but the potassa in the flux enables it to acquire a temperature sufficient for its perfect reduction.

Arsenic is of a steel blue colour, crystalline texture, quite brittle, and of a specific gravity = 8.3. It readily volatilizes, and in close vessels may be distilled at a temperature of 360°,

* This is an extremely useful compound for effecting the reduction of many of the metallic oxides. It consists of charcoal and subcarbonate of potassa, and is best prepared by deflagrating in a crucible a mixture of one part of nitre and two of powdered tartar. The mixture remains in fusion at a red heat, and thus suffers the small globules of reduced metal to coalesce into a button.

which is lower than its fusing point. Its vapour has a very strong and peculiarly characteristic smell, resembling that of garlic. Heated in the air it easily takes fire, burns with a blue flame, and produces copious white fumes of oxide. Exposed to a moist air it gradually becomes incrustated with a gray powder, which is an imperfect oxide, or mixture of metallic arsenic and "arsenious acid. Berzelius found that, in three months, 100 parts of the metal acquired an increase of about 8.5. This metal and all its compounds are virulent poisons.

Native Arsenic has been found in Saxony, Hanover, France, Bohemia, and Cornwall. It usually occurs in rounded masses, or nodules, of a foliated lamellar texture, in the veins of primitive rocks, and is often associated with silver, cobalt, lead, and nickel ores.

Arsenic and Oxygen.—There are two definite compounds of arsenic and oxygen, which are both capable of forming combinations with other metallic oxides. They are sour and soluble in water, and have thence been termed *arsenious* and *arsenic acids*.

The *arsenious acid*, or, as it is commonly called, *white arsenic*, or *white oxide of arsenic*, is the best known, and most commonly occurring compound of this metal; and as cases of poisoning by it are frequent, every person should be well acquainted with its characteristic properties.

Arsenious acid may easily be procured by the combustion of the metal; but as it is formed during certain metallurgic processes, that mode is rarely resorted to. It is abundantly prepared at Joachimsthal in Bohemia, from arsenical cobalt ores, which are roasted in reverberatory furnaces, and the vapours condensed in a long chimney, the contents of which, submitted to a second sublimation, afford the *white arsenic* of commerce.

Arsenious acid generally occurs in white, semi-transparent, brittle masses, of a vitreous fracture. Its specific gravity is 3.72. Its taste is acid, accompanied by a nauseous sweetness, and it is virulently poisonous, producing a set of peculiar symptoms ultimately followed by inflammation and gangrene of the stomach and intestines: it also proves fatal when applied to a wound; and as the local injury is not suffi-

cient to cause death, it is probable that an induced affection of the nervous system and of the heart is the immediate cause of the mischief. (Brodie's *Observations and Experiments on the Action of Poisons*—*Phil. Trans.*, 1812, p. 209.) To get rid of the poison by producing copious vomiting and purging, and to pursue the usual means for subduing and preventing inflammation, are the principal points of treatment to be adopted in cases where this poison has been taken.—Orfila, *Traité des Poisons*, tom. i. p. 123.

By a slow sublimation, arsenious acid forms brilliant octoëdral and tetraëdral crystals: if suddenly heated it runs into a glass; it is volatile at 380° , and has no smell when perfectly free from metallic arsenic. (Paris, *Quarterly Journal of Science and Arts*, vol. vi.) According to Klaproth, 1000 parts of water at 60° , dissolve from two and a half to three of white arsenic; and 1000 parts of water at 212° , dissolve rather more than 77 parts, and about 30 parts are retained in permanent solution. The solutions taste acid and nauseous, and redden litmus, but convert syrup of violets to green. 80 parts of alcohol at 60° , dissolve one part of this acid. Its aqueous solution furnishes tetraëdral and octoëdral crystals by slow evaporation. It also dissolves in oils.

Fischer states that white oxide of arsenic is as such insoluble in water, and that when acted on by water, one portion of the oxide acquires oxygen from the other, and becoming acidified, is rendered soluble: hence, he observes, the undissolved portion loses its colour. (Thomson's *Annals*, vii. 33.) But it may be observed, in opposition to this opinion, that the properties of the solution are not those of arsenic, but of arsenious acid.

The relative proportions of the components of arsenious acid have been variously stated: if we consider Dr. Thomson's experiments as leading to correct results (*Atomic Theory*, i. 235), it consists of 100 arsenic and about 42 oxygen; and, regarding it as composed of 1 proportional of arsenic and 2 of oxygen, the number 38 will be the equivalent of the metal, and arsenious acid will consist of

1 proportional of arsenic	= 38
2 proportionals of oxygen (8×2)	= 16
Equivalent of arsenious acid	= 54

Upon the same authority, the peroxide of arsenic or arsenic acid consists of

1 proportional of arsenic	= 38
3 proportionals of oxygen (8×3)	= 24
Equivalent of arsenic acid	= 62

So that the oxygen in the arsenious acid is to that in the arsenic acid as 2 to 3. The accuracy of this statement, however, is called in question by Berzelius and by Dr. Turner (*Elements of Chemistry*), according to whom, the oxygen in the two acids is in the ratio of 3 to 5: the atomic weight of metallic arsenic was found nearly the same by Thomson and Berzelius; so that the equivalents of the acids will, according to the latter, stand as follow:

1 proportional of arsenic	= 38
$1\frac{1}{2}$ „ oxygen	= 12
Equivalent of arsenious acid	= 50
1 proportional of arsenic	= 38
$2\frac{1}{2}$ „ oxygen	= 20
Equivalent of arsenic acid	= 58

Native White Arsenic occurs in prismatic crystals, and in a pulverulent form: it is found in Saxony and Hungary.

The arsenious acid forms a distinct class of salts, called *arsenites*, which have been but little examined.

The *arsenites of ammonia, potassa, and soda*, are easily soluble and uncrystallizable: they are formed by boiling the acid in the alkaline solutions. Those of *lime, baryta, strontia*, and *magnesia*, are difficultly soluble, and formed in the same way. Arsenite of potassa is the active ingredient in the *liquor arsenicalis* of the *Pharmacopœia*, and in *Fowler's mineral solution* or *tasteless aque drop*.

Arsenite of ammonia produces a yellow precipitate in nitrate of silver, easily soluble in excess of ammonia.

Arsenite of potassa produces a white precipitate in the white salts of manganese; a dingy green precipitate in the solutions of iron; a white precipitate in solutions of zinc and tin. Mixed with a solution of sulphate of copper, a precipitate of a fine apple-green colour falls, called from its discoverer, *Scheele's green*, and is useful as a pigment. In the solutions of lead,

antimony, and bismuth, it forms white precipitates: added to nitrate of cobalt, it forms a pink precipitate; and bright yellow, with nitrate of uranium. With nitrate of silver it forms a white precipitate, soon becoming yellow, and very soluble in ammonia. All these precipitates are probably *arsenites* of the respective metals, and, heated by a blowpipe on charcoal, they exhale the smell of arsenic. They are decomposed when boiled in solution of carbonate of potassa or of soda: they are soluble in excess of arsenious acid, and easily soluble in nitric acid, and such other acids as form soluble compounds with their bases.

Native Arsenite of Lead is found in France, in Spain, and in Siberia.

Arsenic Acid is obtained by distilling a mixture of 4 parts of muriatic and 24 of nitric acid off 8 parts of arsenious acid, gradually raising the bottom of the retort to a dull red heat at the end of the operation. It may also be procured by distilling nitric acid off powdered metallic arsenic.

Arsenic acid is a white substance, of a sour taste; it is deliquescent and uncrystallizable. Its specific gravity is 3.4. It requires for solution 6 parts of cold and 2 of boiling water; its solution reddens vegetable blues, and tastes acid and metallic. Heated to bright redness, it evolves oxygen, and is converted into arsenious acid.

The *Arseniates* are produced by the union of this acid with the metallic oxides; and many which are insoluble may be formed by adding arseniate of potassa to their respective solutions. They are soluble in dilute nitric acid, and in such other acids as do not form insoluble compounds with their bases, and ammonia precipitates them from these solutions. They are readily decomposed by charcoal at a red heat; but many of them when heated alone are unchanged even at a higher temperature. They are decomposed when boiled in solutions of the fixed alkaline carbonates.

Arseniate of Ammonia is formed by saturating arsenic acid with ammonia; prisms and octoëdra are obtained on evaporation, which, when gently heated, effloresce and evolve ammonia: at a higher temperature water is formed, oxide of arsenic sublimes, and nitrogen is evolved, a circumstance first observed by Scheele. It consists of

1	proportional of arsenic acid	.	.	.	=	62
1	„ ammonia	.	.	.	=	17
						<hr/> 79

Binarsenate of Ammonia is formed by adding to a solution of the above crystals one additional proportional of arsenic acid. On evaporation, rhomboidal crystals are deposited, containing, according to Thomson,

2	proportionals of arsenic acid (62×2)	.	.	.	=	124
1	„ ammonia	.	.	.	=	17
2	„ water (9×2)	.	.	.	=	18
						<hr/> 159

Arseniate of Potassa is deliquescent and uncrystallizable.

Binarsenate of Potassa may either be formed by adding excess of arsenic acid to potassa and evaporation; or by heating to redness, in a Florence flask, a mixture of equal parts of nitre and white arsenic; during the latter operation much nitrous gas is evolved, and on dissolving the residue in water, filtering, and evaporating, quadrangular crystals of binarsenate of potassa are obtained. Macquer was the first who thus procured this compound; hence it was termed *Macquer's neutral arsenical salt*. It is not easily decomposed by heat alone, and may be fused and kept red hot without undergoing other change than losing a little acid, but when mixed with about an eighth of charcoal powder and distilled, metallic arsenic rises, and carbonate of potassa, mixed with part of the charcoal, remains in the body of the retort. This salt is used in pharmacy for the cure of agues: it consists of

1	proportional of potassa	.	.	.	=	48
2	proportionals of arsenic acid	.	.	.	=	124
						<hr/> 172

Its crystals contain 2 proportionals of water.

Arseniate of Soda is formed by saturating a solution of carbonate of soda with arsenic acid; on evaporation, rhomboidal crystals are obtained, which effloresce in a dry air. They require, according to Thomson, ten parts of water at 60° , for solution, and the liquid has alkaline properties. When dropped into solutions of earthy and metallic salts, this salt occasions precipitates in most of them, a table of which is given

by Dr. Thomson in the fifteenth volume of the *Annals of Philosophy*. The crystals consist of

1 proportional of soda	=	32
1 „ arsenic acid	=	62
8 proportionals of water (9×8)	=	72
						<hr/>
						166

Binarsenate of Soda is a difficultly crystallizable salt, and very soluble in water. When heated, it does not, like the arseniate, undergo watery fusion. It appears to consist of

1 proportional of soda	=	32
2 proportionals of arsenic acid (62×2)	=	124
5 „ water (9×5)	=	45
						<hr/>
						201

Arseniate of Lime is deposited when arsenic acid is dropped into lime-water, or when arseniate of potassa is added to nitrate of lime; it is difficultly soluble in water, and consists of

1 proportional of arsenic acid	=	62
1 „ lime	=	28
						<hr/>
						90

Arseniate of lime may also be formed by heating a mixture of white arsenic and quicklime, in which case, as Dr. Wollaston first observed, when it has attained a certain temperature ignition suddenly ensues, and metallic arsenic sublimes; so that one portion of the arsenious acid confers oxygen upon the other, to convert it into arsenic acid.

Arseniate of Baryta may be formed by mixing arseniate of potassa with nitrate of baryta; when the acid is not in excess it is insoluble in water. It may be considered as a compound of 1 proportional of acid = 62 + 1 of baryta = 78.

Arseniate of Strontia.—When solutions of nitrate of strontia and arseniate of soda are mixed in atomic proportions, no immediate precipitate appears, but in twenty-four hours small crystals are formed, which are minute rectangular four-sided prisms, tasteless, not affecting vegetable blues, and very sparingly soluble in water. They consist of

1 proportional of strontia	=	52
1 „ arsenic acid	=	62
8 proportionals of water (9×8)	=	72
						<hr/>
						186

Arseniate of Magnesia is soluble, deliquescent, and uncrySTALLIZABLE, when there is an excess of acid: but a very difficultly soluble, and neutral arseniate may be obtained, partly in powder and partly in tufted crystals, by mixing dilute solutions of sulphate of magnesia and arseniate of soda in atomic proportions, and suffering them to remain at rest for twenty-four hours. The crystals consist, according to Thomson, of

1 proportional of magnesia	= 20
1 „ arsenic acid	= 62
8 proportionals of water (9×8)	= 72
					<hr/> 154

Dried at a temperature of 500° , they lose 6 proportionals of water, but still retain 2, which are disengaged at a red heat.

Arseniate of Manganese is precipitated in the form of a white powder, when arseniate of potassa is added to muriate of manganese. When dried at a high temperature, it loses water, and consists of

1 proportional of oxide of manganese	.	.	.	= 36
1 „ arsenic acid	.	.	.	= 62
				<hr/> 98

Arseniate of Iron.—Arseniate of ammonia, added to the solutions of protosulphate and persulphate of iron, occasions greenish precipitates of *protarseniate* and *perarseniate* of iron, both of which have been examined by Mr. Chenevix.—*Phil. Trans.*, 1801, pp. 220, 225. The *native arseniate of iron* which is found in small cubes of a dark green colour, and a specific gravity of 3., appears to consist of

1 proportional of arsenic acid	.	.	.	= 62
2 proportionals of protoxide of iron (36×2)	.	.	.	= 72
3 „ water (9×3)	.	.	.	= 27
				<hr/> 161

Arseniate of Zinc is precipitated in a white gelatinous state, when arsenic acid, or an alkaline arseniate, is added to sulphate of zinc. It consists of

1 proportional of oxide of zinc	.	.	.	= 42
1 „ arsenic acid	.	.	.	= 62
				<hr/> 104

Arseniate of Tin is a white insoluble powder, precipitated by adding arseniate of potassa to muriate of tin.

Arseniate of Copper is formed by adding an alkaline arseniate to nitrate of copper; it is a blue insoluble powder, and when dried at a temperature not exceeding 212° , appears to consist of

1 proportional of peroxide of copper	.	.	.	=	80
1 " arsenic acid	.	.	.	=	62
4 proportionals of water (9×4)	.	.	.	=	36
					<hr/>
					178

It is, therefore, a hydrated subperarseniate. The arseniates of copper have been submitted to an elaborate investigation by Mr. Chenevix (*Phil. Trans.*, 1801); he has described five varieties, as shown in the following table.—Thomson's *System*, ii. 616.

Variety	1st	.	.	.	Acid.	1.	.	.	.	Oxide.	3.70	.	.	.	Water.	2.50
"	2d	.	.	.	1.	2.76	1.	
"	3d	.	.	.	1.	1.72	0.70	
"	4th	.	.	.	1.	1.80	0.53	
"	5th	.	.	.	1.	0.88	0.60	

These numbers cannot, without great violence, be rendered consistent with the theory of proportionals.

Arseniate of Antimony.—Nothing is known respecting the combinations of arsenic acid with the oxides of antimony.

Arseniate of Bismuth falls as an insoluble white powder on adding arsenic acid to nitrate of bismuth: when dry it consists of

1 proportional of oxide of bismuth	.	.	.	=	80
1 " arsenic acid	.	.	.	=	62
					<hr/>
					142

Arseniate of Cobalt is precipitated of a red colour by the addition of an alkaline arseniate to a soluble salt of cobalt: deprived of water, it consists of

1 proportional of oxide of cobalt	.	.	.	=	38
1 " arsenic acid	.	.	.	=	62
					<hr/>
					100

Arseniate of Uranium is thrown down of a straw colour when arseniate of potassa is added to nitrate of uranium.

Several of the metallic arseniates are found *native*; of these the most important are—1. The *arseniate of iron*, which occurs in Cornwall, usually in cubic crystals of various shades

of green. 2. *Arseniate of copper*, of which there are two principal varieties, the green and blue. The green is found in flattened octoëdra, in hexaëdral tables, and in prisms with dihedrals summits. Sometimes it is massive, or fibrous, and radiated. The blue variety is tetrahedral, octoëdral, and rhombic. These beautiful minerals are almost peculiar to Cornwall. 3. *Arseniate of Lead* occurs in small hexaëdral crystals, of a yellow, green, or brown colour, transparent, and of a resinous lustre. It has been found in Cornwall, France, and Spain. 4. *Arseniate of cobalt*, or *peachblossom cobalt ore*, is a rare mineral found in Saxony and Cornwall.

Arsenic and Chlorine.—*Chloride of arsenic* is formed by throwing finely-powdered arsenic into chlorine; the metal burns and forms a whitish deliquescent and volatile compound; it may also be obtained by distilling six parts of corrosive sublimate with one of powdered arsenic; the chloride passes into the receiver in the form of an unctuous fluid, formerly called *butter of arsenic*. A preferable process for obtaining this compound is that of M. Dumas (*Ann. de Chim. et Phys.*, xxxiii. 360). One part of arsenious acid with ten parts of sulphuric acid, are put into a tubulated retort, and the temperature raised to about 212°. Fragments of fused common salt are then to be thrown in by the tubulature; by continuing the heat, and successively adding the salt, chloride of arsenic is obtained; it distils over, and may be condensed in cold vessels. Very little muriatic acid is disengaged, but towards the end of the operation, a portion of hydrated chloride of arsenic is produced, which floats upon the pure chloride, and appears more viscid and colourless: it may be deprived of water by redistillation with concentrated sulphuric acid. Mixed with a larger quantity of water, the chloride of arsenic is decomposed, and white oxide or arsenious acid is formed, muriatic acid being at the same time produced. Hence it may be inferred, that the chlorine is to the arsenic in the same proportion as the oxygen in the arsenious acid; but the exact composition of the chloride has not been satisfactorily ascertained.

Chlorate of Arsenic has not been examined.

Iodide of Arsenic, obtained by heating the metal with excess of iodine, is of a deep red colour, and volatile. When acted upon by water, it produces hydriodic and arsenious

acids, whence it appears probable that its composition is analogous to that of the chloride.

The action of iodic acid and of bromine and fluorine on arsenic has not been examined.

Arsenic and Hydrogen—Arsenuretted Hydrogen Gas.—When arsenic is presented to nascent hydrogen, a portion of the metal combines with the gas. The compound is best obtained by adding a portion of metallic arsenic, or of white arsenic, to the mixture of zinc filings and dilute sulphuric acid, usually employed for the production of hydrogen. The gas may be collected over water, by which it is not sensibly absorbed.

Arsenuretted hydrogen may also be obtained by the action of the following alloy upon water. Mix two parts of antimony with two of cream of tartar, and one of white arsenic, and heat the mixture strongly for two hours in a covered crucible. When cold, a button of the triple alloy of potassium, antimony, and arsenic will be obtained, fragments of which may be transferred under a jar inverted in water (*Quarterly Journal*, xiii. 225).

Great care should be taken to avoid the deleterious effects of this gas; it proved fatal to the late M. Gehlen. (*Ann. de Chim. et Phys.*, iii. 135.)

The specific gravity of this gas is liable to vary according to the mode by which it is procured. I have always found it heaviest when obtained from a mixture of 4 parts of zinc, 1 of arsenic, and 3 of sulphuric acid, diluted with 4 or 5 of water. After standing a day over water, it deposits a small quantity of brown matter, which appears to be a *hydruret of arsenic*. It is probable that the gas, hitherto described under the name of arsenuretted hydrogen, is a mixture of the real compound with hydrogen.

The gas obtained by the above-described processes deposits arsenic at high temperatures: exposure to intense cold is said to occasion its liquefaction. It smells strongly alliaceous; it extinguishes a taper, and burns with a pale blue flame, depositing arsenic and its oxide. It is not absorbed to any extent by water, and has no effect upon vegetable blue colours. If detonated with oxygen, arsenious acid and water are formed. According to Stromeyer (*Nicholson's Journal*, vol. xix.), it

requires for its perfect combustion 0.72 parts of its bulk of oxygen ; but this is probably not sufficient to burn the arsenic. If it be regarded as a compound of 1 volume of hydrogen and 1 volume of the vapour of arsenic, the 2 being condensed into 1, its specific gravity to hydrogen would be 39 to 1, and to air 2.708 to 1 ; and 100 cubical inches would weigh 82.604 grains.

If bubbles of chlorine be passed up into a jar of arsenuretted hydrogen, standing over warm water, flame and explosion are often produced, muriatic acid is formed, and a brown hyduret is deposited ; but if the gas be passed in the same way by successive bubbles into chlorine, no inflammation results, absorption takes place, and muriatic acid and chloride of arsenic are formed. If the chlorine be not very pure, and when the gases are cold, inflammation seldom follows their mixture. Chlorine, added to a mixture of sulphuretted with arsenuretted hydrogen, causes a deposit of sulphuret of arsenic. Nitric acid suddenly decomposes arsenuretted hydrogen ; water, oxide of arsenic, nitrous acid, and nitric oxide are the results.

Hyduret of Arsenic is a brown compound, obtained by negatively electrifying arsenic in contact with water ; or by acting upon water by an alloy of potassium and arsenic. It has not been analysed.

Arsenic and Sulphur.—By slowly fusing a mixture of metallic arsenic and sulphur, or by heating white arsenic with about half its weight of sulphur, a *red sulphuret of arsenic* is obtained. It is crystallizable, and of a vitreous fracture : its specific gravity is 3.4. It may be sublimed, unaltered, in close vessels. It is composed of

1 proportional of arsenic	= 38
1 " sulphur	= 16
					<hr/> 54

It is usually known under the name of *Realgar*, and occurs *native* in Germany and Switzerland, in veins of primitive rocks and among volcanic matter. Its primitive form is an acute octoëdron.

If white arsenic be fused with its weight of sulphur, or if it be dissolved in water and precipitated by a current of sulphuretted hydrogen gas, a fine yellow sulphuret of arsenic falls,

which is usually called *Orpiment*. It is fusible, and assumes a crystalline texture on cooling, and may be sublimed without decomposition in close vessels. It dissolves in the caustic alkalis. Orpiment is a *sesquisulphuret* of arsenic, containing

1	proportional of arsenic	= 38
$1\frac{1}{2}$	„ sulphur	= 24
						<hr/> 62

These sulphurets are readily decomposed by fusion with potassa; sulphuret of potassium and a sublimate of metallic arsenic are the results.

Native Orpiment is of a bright lemon or golden colour. It is generally massive and lamellar. It occurs both in primitive and secondary rocks in Suabia, Hungary, China, and South America.

M. Braconnot has successfully employed an *ammoniacal solution of sulphuret of arsenic* as a dye stuff; the process he recommends is as follows: 1 part of sulphur, 2 of white arsenic, and 5 of pearlash, are to be fused in a crucible at a heat a little below redness: a yellow mass results, which is to be dissolved in hot water and filtered; the filtered solution, diluted with water, is to be treated with weak sulphuric acid, and will give a fine yellow precipitate, which easily dissolves in ammonia, forming a solution at first yellow, but becoming colourless on adding more ammonia. The wool, silk, cotton, or linen, is to be dipped into this solution, more or less diluted according to the colour required, care being taken that no metallic vessels are used; on taking them out they are at first colourless, but, as the ammonia evaporates, become yellow; they are then to be freely exposed to the air, washed, and dried. This colour is very permanent, but soap impairs it. Orpiment is also the basis of the pigment called *King's Yellow*.

When sulphuretted hydrogen is passed through a solution of arsenic acid, a yellow precipitate falls, which resembles orpiment in colour, and, like it, may be sublimed without change, in close vessels; it also is easily fusible and soluble in alkaline solutions. It is probably proportional in composition to the arsenic acid, and therefore consists, either of one proportional of arsenic and three of sulphur, or of one and two and a half.

The sulphurets of arsenic are all poisonous, though less virulent than the oxides. (Orfila.)

Sulphuret of Arsenic and Iron is found native in many parts of Europe. It is of a more silvery colour than iron pyrites, and when heated exhales the odour of arsenic. It is called *arsenical pyrites*, or *mispickel*.

Phosphuret of Arsenic is formed by heating the metal, or its oxide, with phosphorus; it is gray and brittle.

Alloys of Arsenic.—Arsenic forms alloys with most of the metals, and they are generally brittle. With potassium it forms a brownish compound, which, when put into water, evolves less hydrogen than pure potassium, in consequence of the formation of hyduret of arsenic. With sodium, the alloy is either brown and of an earthy aspect, or gray and metallic, according to the proportions of the metals: water acts upon it as upon the former. (Gay-Lussac and Thenard. *Recherches Physico-Chimiques*, tom. i.) The alloy of arsenic and manganese is not known. With iron, zinc, and tin, it forms white brittle compounds; with copper it forms a white malleable alloy; with lead, a brittle compound of a lamellar texture; with antimony, the alloy is brittle, hard, and very fusible. It combines with bismuth, and probably with cobalt, but these alloys have not been examined.

The separation of arsenic from other metals may generally be accomplished by repeated deflagration with nitre, by which it is acidified, and the arseniate of potassa may afterwards be washed out by hot water; but by some of the metals it is very obstinately retained.

As arsenic, either accidentally or intentionally taken, is a very frequent cause of death, and often the subject of judicial inquiry, it becomes of importance to point out the most effectual modes of discovering its presence. Where arsenic proves fatal, it is very seldom found in the contents of the stomach after death, but is generally previously voided by vomiting or by stool; and we often can detect it in the matter thrown off the stomach, in the form of a white powder, subsiding in water. The inflammation of the stomach which results is generally a secondary effect, and takes place equally, whether the poison be swallowed or applied to a wound. If minute quantities of white powder be detected, however, in the stomach after death, or in the matter vomited, it is to be carefully collected, and treated as follows:

(a.) Mix a small portion of it with about two parts of black flux; introduce the mixture into a glass tube, and gradually heat it red-hot in the flame of a spirit-lamp. If arsenic be present, a *steel-coloured sublimate* will attach itself to the cooler part of the tube, which, heated in contact of air, evaporates in a *white smoke, strongly smelling of garlic*.

(b.) Boil the suspected matter in a little distilled water; and when the solution has cooled, add a strong solution of sulphuretted hydrogen, or pass the gas through it. If arsenic be present, a *yellow precipitate* will appear. According to Dr. Ure, $\frac{1}{100000}$ of arsenious acid may be detected in water by this test. The hydrosulphuretted alkalis do not affect the arsenious solution unless a drop or two of nitric or muriatic acid be added when the yellow precipitate falls; these tests are, however, equivocal where very small quantities are to be detected; if a slight excess of alkali be accidentally present, it retains the sulphuret in solution, and excess of acid occasions a little sulphur to fall.

(c.) To the solution *b* add a drop of solution of subcarbonate of potassa, and then a drop or two of solution of sulphate of copper. An *apple-green precipitate*, commonly known as *Scheele's Green*, indicates arsenic. The ammonio-sulphate and ammonio-acetate of copper also give the peculiar green precipitate when added to very dilute solutions of white arsenic. This test, however, is fallacious when applied to mixed fluids, for Dr. Christison has shown that the ammoniacal solution of sulphate of copper produces in some vegetable and animal infusions, containing no arsenic, a greenish precipitate, which may be mistaken for Scheele's green; whereas, in other mixed fluids, such as tea and porter, to which arsenic has been added, it occasions none at all if the arsenious acid is small in relative quantity. In some of those liquids a free vegetable acid may be the solvent, but the arsenite of copper is also dissolved by tannin, and perhaps by other vegetable, as well as some animal principles. (Turner.)

(d.) Add to the solution *b* a drop of nitrate of silver, and of solution of ammonia. A *yellow precipitate* indicates arsenic.

(e.) The Voltaic battery made to act by two wires on a little arsenious solution placed upon a piece of glass, develops metallic arsenic at the negative pole; and if this wire be of copper it becomes whitened.

It must be observed, in regard to these tests, that the first only is unequivocal, and that the appearances produced by the others may originate from the presence of other substances. When, however, all the above appearances ensue, no doubt of the existence of arsenic can be entertained. The several precipitates should be collected, and will, when placed upon a red-hot iron, exhale the peculiar smell of arsenic. The reader is referred for further particulars on this subject to Henry's *Elements of Chemistry*, vol. ii. p. 480, 8th edit.; to Murray's *System*, vol. iii. p. 441, 4th edit.; to Dr. Bostock's *Paper* in the *Edinb. Med. and Surg. Journal*, vol. v. p. 166; to Mr. Hume's *Essay*, in the *Phil. Mag.* vol. xxxiii.; and *London Med. and Phys. Journal*, vol. xxiii.; to Dr. Marcet's *Paper* in the *Medico-Chirurgical Transactions*, vol. ii.; to Mr. Sylvester's *Observations* in Nicholson's *Journal*, vol. xxxiii.; to Ure's *Dictionary*—art. ACID (ARSENIOUS); and to Orfila's work on *Poisons*. See also the *Edinburgh Medical and Surgical Journal* for 1824; and the *Transactions of the Medico-Chirurgical Society of Edinburgh*, vol. ii.

Section XXIII. MOLYBDENUM.

THE sulphuret is the most common natural compound of this metal. To procure the metal, the native sulphuret is powdered and exposed under a muffle, moderately heated, till converted into a gray powder, which is to be digested in ammonia, and the solution filtered and evaporated to dryness. The residuum is dissolved in nitric acid, re-evaporated to dryness, and violently heated with charcoal. Metallic molybdenum may also be obtained by passing a current of dry hydrogen gas over molybdic acid, strongly heated in a porcelain tube. It should be suffered to cool in the contact of hydrogen.

The metal is of a whitish gray colour, and of excessively difficult fusion. According to Hielm, its specific gravity is 7.4; according to Bucholz, it is as high as 8.6. When exposed

to heat and oxygen, molybdenum is acidified, a white crystalline sublimate of *molybdic acid* being formed.

Oxides of Molybdenum.—This metal forms three oxides, two of which are salifiable, and the third an acid.

Protoxide of Molybdenum is obtained, according to Berzelius, by precipitating the muriatic solution of molybdic acid by zinc. It is in the form of a brown hydrate, and gives dark-coloured solutions with the acids. Its salts have not been very satisfactorily examined.

Deutoxide of Molybdenum was obtained by Bucholz, by strongly heating molybdate of ammonia, rammed down in a crucible: the molybdic acid is reduced by the hydrogen of the ammonia, and a crystalline copper-coloured substance is obtained, of the specific gravity 5.6. It may be procured, according to Berzelius, by heating a mixture of muriate of ammonia and molybdate of soda in a platinum crucible till the fumes cease: the residue is well washed, digested in caustic potassa to separate any molybdic acid, and again washed with boiling water. The oxide remains in the form of a black powder, becoming dark brown when dry, and purple when exposed to the sun's rays. In this state it is almost insoluble in acids and alkalis, and nitric acid converts it into molybdic acid.

The *Hydrated Deutoxide* may be obtained by digesting a mixture of molybdic acid and metallic molybdenum in muriatic acid, till the solution, which is at first blue, becomes dark-red: the addition of ammonia then precipitates the hydrate, in colour resembling peroxide of iron. In this state it dissolves in the acids, and forms reddish-brown solutions.

When metallic molybdenum and molybdic acid are boiled together in water, a blue solution is formed, which has sometimes been termed *molybdous acid*, but which appears to be a compound of molybdic acid with the deutoxide, and consequently a *molybdate of molybdenum*.

Peroxide of Molybdenum, or Molybdic Acid. To obtain this acid, the native sulphuret of molybdenum should be triturated, to reduce it, as far as possible, to powder, and distilled, with three or four parts of nitric acid, to dryness. This operation should be repeated, till the ore is converted into an uniform white mass, which consists of molybdic, nitric, and

sulphuric acids; the two latter may be expelled by a red heat, in a platinum crucible, and the remaining molybdic acid repeatedly washed with boiling water, in which it is little soluble, will be nearly pure. It may be rendered perfectly pure by solution in ammonia, precipitation by nitric acid, and exposure to heat.

The molybdic acid, thus procured, is a white powder, of the specific gravity of 3.46, and requiring 960 parts of boiling water for its solution, which is yellow, reddens litmus, but has no sour taste. Heated to redness in an open vessel, it slowly sublimes, and condenses in brilliant yellowish scales. It dissolves in hot sulphuric acid, forming a solution, which is colourless while hot, but on cooling acquires a blue colour, which is heightened by the addition of soda. Its muriatic solution is pale yellowish green, but becomes blue when saturated by potassa.—Hatchett, *Phil. Trans.* 1796.

Assuming the molybdic acid to be a compound of one proportional of molybdenum and three of oxygen, the number 48 will be the equivalent of the metal, and those of the oxides as follow:—

1 proportional of molybdenum	.	.	.	= 48
1 „ oxygen	.	.	.	= 8
Equivalent of the protoxide	.	.	.	= 56
1 proportional of molybdenum	.	.	.	= 48
2 proportionals of oxygen (8×2)	.	.	.	= 16
Equivalent of the deutoxide	.	.	.	= 64
1 proportional of molybdenum	.	.	.	= 48
3 proportionals of oxygen (8×3)	.	.	.	= 24
Equivalent of molybdic acid	.	.	.	= 72

Molybdate of Ammonia is not crystallizable, and when heated to redness the ammonia is driven off, and the acid converted into oxide of molybdenum.—Bucholz, *Gehlen's Journal*, iv. 616.

Molybdate of Potassa is formed by digesting the acid in potassa; or by heating to redness two parts of nitre with one of molybdic acid, and lixiviating the mass. Its solution, which is colourless, yields small rhomboidal crystals by evaporation, and affords a precipitate of molybdic acid, to muriatic, nitric, and sulphuric acids.

Molybdate of Soda is more soluble than molybdate of potassa, and furnishes permanent and transparent crystals. In obtaining both these salts, a deposit of a yellowish powder ensues, which is probably a *bimolybdate* of potassa and of soda.

Native Molybdate of Lead occurs principally in crystals of different shades of yellow. It was first discovered in Carinthia, and has since been found in Mexico, Hungary, and Saxony. According to Mr. Hatchett's analysis (*Phil. Trans.* 1796) it contains 38 molybdic acid + 58.4 oxide of lead; and these numbers closely correspond with its theoretical composition, which should be 1 proportional of molybdic acid = 72 + 1 proportional of oxide of lead = 112.

Molybdate of Silver, of Mercury, of Lead, and of Nickel, may be procured by adding molybdic acid to the respective nitrates of those metals.

The remaining molybdates have either not been examined, or the accounts of their properties are too much at variance to be depended upon.

Chloride of Molybdenum.—When the finely-divided metal is heated in chlorine, a very deep-coloured red vapour rises, and condenses in crystals, much resembling iodine in appearance, easily fusible, very volatile, and deliquescing in the air into a dark red or yellow fluid: when acted on by water, much heat is extricated, and the dilute solution has a green or blue colour.

Perchloride of Molybdenum is formed by gently heating the deutoxide of molybdenum in a stream of chlorine; molybdic acid is formed, and a white crystallized sublimate, which is the perchloride.

Iodide of Molybdenum is a dark-red compound.

Fluoride of Molybdenum is a black crystalline substance, forming a red aqueous solution. It is obtained by dissolving the hydrated deutoxide in hydrofluoric acid, and evaporating to dryness.

Sulphuret of Molybdenum is a sectile compound of a metallic lustre.

The *Native Sulphuret* is found in Bohemia, Sweden, and near Mont Blanc, disseminated in a gray granite. It has been found in England, chiefly in Cornwall; and in Scotland, in Inverness-shire. It rarely occurs crystallized; generally

massive, and made up of easily separable laminae. It is soft and unctuous to the touch, and in colour much like lead. It is found exclusively in primitive rocks; generally in granite, and with quartz. From the experiments of Bucholz, it appears to be a bisulphuret, composed of

1 proportional of molybdenum	.	.	= 48
2 proportionals of sulphur (16 × 2)	.	.	= 32
			<hr/> 80

Section XXIV. CHROMIUM.

CHROMIUM was discovered by Vauquelin in 1797. It may be obtained by intensely igniting its oxide with charcoal. Its colour resembles that of iron, and its specific gravity is 5.9. It is brittle, and difficult of fusion, and has only been imperfectly examined.

Chromium and Oxygen. — There are two well-defined oxides of chrome: the *protoxide*, which is a salifiable base, and the *peroxide* or *chromic acid*. When chromium is exposed to the action of heat and air, it combines with oxygen, and a *protoxide* is formed. One of the simplest methods of obtaining it consists in heating chromate of mercury red hot: it may also be obtained by calcining a mixture of equal parts of chromate of potassa and sulphur in a close earthen crucible, at a red heat, and washing the green mass which is produced, to dissolve out the sulphate and sulphuret of potassa: the oxide of chromium remains, and is rendered pure by repeated washings. (*Ann. de Chim. et Phys.* xiv. 299.) Protoxide of chromium is of a green colour, infusible and unchanged by heat. After exposure to a red heat it is scarcely attacked by the acids, but readily dissolves in them when recently precipitated and in the state of hydrate. It is converted into chromic acid by deflagration with nitre. Fused with vitrifiable substances, and especially with borax, it confers upon them a characteristic green colour: hence its use in porcelain and enamel painting.

Hydrated Oxide of Chrome is precipitated from its acid solutions, by the alkalis, in the form of a bulky green powder. It may be best obtained by adding a mixture of equal parts

of muriatic acid and alcohol, in small portions, to a boiling solution of chromate of potassa, until the liquid acquires a pure green colour. When cold, excess of ammonia is added, which precipitates the oxide, combined with a large relative proportion of water; and in this state it readily dissolves in the acids. (Thomson.)

Native Protoxide of Chromium has been found in France, in the department of the Rhone, in the form of a green incrustation. It is the colouring matter of the emerald, and exists in a few other minerals.

When nitrate of chromium is decomposed at a red heat, an insoluble *brown deutoxide* is formed. It does not dissolve in the acids; but when heated with muriatic acid, chlorine is evolved, and a muriate, containing the protoxide, is formed.

Peroxide of Chromium, or *Chromic Acid*, is most easily procured by the decomposition of the native *chromate of lead*, which may be effected by reducing it to a very fine powder, and boiling it in a solution of potassa or soda. An orange-coloured solution of the alkaline chromate is thus formed, to which sulphuric acid is to be added. On evaporation crystals of chromic acid are formed, along with the sulphate of soda or of potassa. Or the acid may be obtained by adding nitrate of baryta to the chromate of potassa, and subsequently decomposing the chromate of baryta which falls by sulphuric acid. In these cases, however, according to M. Gay-Lussac, the red crystals that are obtained contain sulphuric acid, and are therefore a combination of the two acids, or a persulphate of chromium. (*Ann. de Chim.* xvi. 103.)

Pure chromic acid may be procured, according to Unverdorben, by the following process, from the ore called *chromate of iron*, which is a more common mineral than the chromate of lead. It is a compound of the oxides of iron and chromium. Reduce it to a fine powder, and expose it to a bright red heat for two hours, mixed with half its weight of nitre; wash the contents of the crucible, and add to the lixivium nitric acid sufficient to neutralize the excess of potassa: in this way a solution of nitrate and of chromate of potassa is obtained. Upon adding nitrate of lead to this solution, *chromate of lead* is precipitated in the form of a yellow powder, which is to be washed, dried, and heated to redness. Of this chromate, four

parts are then well mixed with three of finely powdered and pure fluor spar (previously heated red-hot), and five of highly concentrated sulphuric acid; this mixture is introduced into a distillatory apparatus of lead or platinum, and gently heated; a red vapour is liberated, which is conducted into distilled water contained in a vessel of platinum: it is then condensed into a dark orange-coloured liquid: the red vapour is a *fluoride of chromium*, and is resolved by water into hydrofluoric and chromic acids, the solution of which, evaporated in a platinum vessel, leaves pure chromic acid. If, instead of conducting the vapour into water, it be received into a platinum vessel, containing pieces of moist blotting-paper, it is decomposed as before; but the chromic acid is deposited in beautiful acicular crystals, which soon deliquesce.

Chromic acid is of a dark red colour; its taste is sour and metallic; it tinges the cuticle yellow; it may be obtained from its aqueous solutions in deliquescent prismatic crystals, of a ruby colour. When heated red-hot, it gives out a portion of oxygen, and becomes the green protoxide; it is energetically acted on and converted into oxide by ammonia. It dissolves in alcohol, and the solution gradually deposits green oxide. It combines with sulphuric acid, and the compound forms octoëdral crystals, formerly mistaken for pure chromic acid. With muriatic acid it forms a compound which dissolves gold. The aqueous solution of chromic acid is decomposed by the sun's rays, and deposits the oxide. Chromic acid appears to be the colouring matter of the ruby.

Native Chromite of Iron has been found in small crystalline grains, of an octoëdral form. It commonly occurs massive, of a black colour, with a slight metallic lustre, and hard enough to scratch glass. It has been found in Siberia, France, and America, and at Unst in Shetland.

Native Chromate of Lead is a very rare mineral, hitherto only found in the Uralian mountains in Siberia; it occurs in prismatic crystals, of a fine orange-red colour, and is occasionally accompanied by small green crystals, supposed to be *chromite of lead*, or a combination of oxide of chrome and oxide of lead.

Satisfactory experiments on the composition of the oxides of chromium are still wanting. According to Berzelius, the

green oxide of chromium contains half the quantity of oxygen existing in the chromic acid; and from his statement, the number 28 may be assumed as the equivalent of the metal, and the protoxide and the acid will be constituted as follow :—

1 proportional of chromium	.	.	.	= 28
1 „ oxygen	.	.	.	= 8
Equivalent of protoxide of chromium				<hr/> = 36
1 proportional of chromium	.	.	.	= 28
2 proportionals of oxygen (8×2)	.	.	.	= 16
Equivalent of chromic acid				<hr/> = 44

Dr. Thomson says that the equivalent of chromic acid is 52; and that of the metal 32; and that the protoxide consists of one proportional of metal and one of oxygen ($32 + 8$); and the acid of one proportional of metal and two and a half of oxygen ($32 + 20$). Some regard the acid as constituted of one proportional of chromium and three of oxygen ($28 + 24$). This gives 52 as the equivalent of the acid.

Chloride of Chromium is formed by boiling chromic acid with excess of muriatic acid, evaporating to dryness, and heating the residue out of the contact of air. When a mixture of common salt and bichromate of potassa are fused together, and the mass broken into pieces, and distilled with anhydrous sulphuric acid, a red vapour, condensing into a liquid, is produced, which is a *perchloride of Chromium*. It at first sinks in water, but afterwards acts energetically upon it, and becomes chromic and muriatic acids.

The *Iodide* and *Bromide of Chromium* have not been examined.

Fluoride of Chromium has been above noticed in describing the preparation of chromic acid.

Combinations of Chromic Acid.—The chromates of ammonia, potassa, soda, lithia, lime, and magnesia are soluble and crystallizable, and of an orange colour. The chromates of baryta and strontia are difficultly soluble, and may be formed by adding chromate of potassa or soda to their soluble saline compounds. The other insoluble metallic chromates may be formed in the same way, and their colours, which are various and beautiful, often enable us to judge of the nature of the metal present. Thus chromate of soda forms insoluble preci-

pitates in solutions of silver, mercury, lead, copper, iron, and uranium; the colours are crimson, red, orange, or yellow, apple-green, brown, and yellow. It forms no precipitate in solutions of nickel, zinc, tin, cobalt, gold, or platinum; whence, perhaps, it may be inferred, that the chromates of the latter metals are soluble.

The chromates are decomposed by muriatic, nitric, and sulphuric acids. Muriatic acid, heated with the chromates and a little alcohol, evolves chlorine, and the chromic acid is reduced to the state of oxide.

Chromate of Potassa forms yellow crystals, the primary form of which is a right rhombic prism. (*Ann. of Phil.* vi. 120.) It has a disagreeable metallic taste. It is extremely soluble in boiling water. At 60° , 100 parts of water dissolve about 48 of the salt. It is insoluble in alcohol. According to Thomson, it is anhydrous, and consists of

1 proportional of chromic acid	= 52
1 ,, potassa	= 48
	<hr/>
	100

Bichromate of Potassa is obtained by adding a sufficiency of sulphuric acid to a solution of the chromate to give it a sour taste, and setting it aside for a day or two, when orange-coloured crystals are deposited, composed of

2 proportionals of chromic acid (52×2)	= 104
1 proportional of potassa	= 48
	<hr/>
	152

When the yellow or neutral *chromate of lead* is boiled with potassa, a *subchromate of lead* is formed, of a very fine red colour, composed, as has been shown, by Mr. Badams (*Ann. of Phil.*, N. S. ix. 303), of 1 proportional of chromic acid + 2 oxide of lead, or 18.84 acid, 81.16 oxide: whereas the yellow chromate contains 1 proportional of acid + 1 oxide, or *per cent.* 31.7 acid, 68.3 oxide. The subchromate is a valuable oil and water colour, and has been successfully applied to calico printing, being produced by nitrate of lead and an alkaline solution of chromate of potassa.

Artificial chromate of lead is also an excellent yellow pigment either for water or oil painting; it has been used by M. Lassaigne as a dye-stuff applicable to linen, cotton, silk, and

wool (*Ann. de Chim. et Phys.* xv. 76), and is a source of a fine yellow in calico printing. The chromates of lead are soluble in caustic potassa, and readily decomposed by a mixture of muriatic acid and alcohol. Muriatic ether, chloride of chromium, and chloride of lead, are the results.

Nitrate of Chromium is a soluble green salt.

Sulphuret of Chromium may be formed as follows: Mix chloride of chromium with five times its weight of sulphur, and heat the mixture to whiteness in a bent glass tube: the sulphuret thus obtained is gray and unctuous like plumbago: exposed to a red heat, the sulphur burns off, and green oxide of chrome remains. Nitric acid does not act readily upon it, but nitromuriatic acid dissolves it. It consists of

Chromium	100
Sulphur	10.5

LASSAIGNE, *Ann. de Chim. et Phys.*, xiv. 299.

Sulphite and Sulphate of Chromium are soluble green salts.

Potassa-sulphate of Chromium.—When a mixed solution of sulphate of chromium and sulphate of potassa, acidulated by sulphuric acid, is subjected to very slow evaporation, octoëdral crystals of a greenish-purple colour are formed.

Sulpho-chromate of Potassa is obtained by mixing solutions of chromate and sulphate of potassa: it forms greenish-yellow octoëdral crystals, which are anhydrous, and consist of 6 proportionals of sulphate of potassa + 1 chromate of potassa. (Thomson.)

Phosphuret of Chromium is formed by strongly heating a mixture of phosphate of chromium and charcoal; it is of a gray colour.

Phosphate of Chromium is of a green colour, and soluble in excess of acid.

Carbonate of Chromium has not been formed; but when carbonated alkalis are added to the salts of oxide of chromium, the precipitate consists of a mixture of subcarbonate and hydrated oxide of chromium.

Section XXV. TUNGSTEN.

THIS metal, which has also been called *Scheelium* and *Wolframium*, is obtained by exposing a mixture of tungstic acid and charcoal to a red heat, or by passing hydrogen over the ignited acid. It is difficult of fusion, very hard, brittle, and of an iron colour. Its specific gravity 17.5. By the action of heat and air, tungsten is converted into an oxide, which is of a yellow colour. It is also oxidized by nitric acid. It is gradually dissolved by solution of potassa, with the evolution of hydrogen, and a tungstate of potassa is produced.

Oxides of Tungsten.—This metal is susceptible of two degrees of oxidizement, and forms an oxide and an acid; according to Berzelius, the oxygen in the former is to that in the latter in the ratio of 2 to 3, and if 96 be assumed as the equivalent of the metal, the protoxide will consist of

1 proportional of tungsten	.	.	.	= 96
2 „ oxygen (8 × 2)	.	.	.	= 16
				<hr/> 112

And tungstic acid, according to Bucholz, of

1 proportional of tungsten	.	.	.	= 96
3 „ oxygen (8 × 3)	.	.	.	= 24
				<hr/> 120

There are two native combinations of tungsten, which are resorted to as sources of the metal: these are *Wolfram* and *Tungstate of Lime*.

Wolfram is found in primitive countries generally accompanying tin ores; its colour is brownish black: it occurs massive and crystallized, its primitive form being a rectangular parallelepiped. It abounds in Cornwall. It consists of tungstic acid united with oxides of iron, and manganese.—Thomson's *Annals*, vi. 198.

Native Tungstate of Lime is a whitish semitransparent substance, found in England, Saxony, Bohemia, and Sweden, and occurring crystallized and massive. Its most usual form is the octoëdron.

Oxide of Tungsten may be obtained by mixing finely powdered wolfram with twice its weight of carbonate of potassa, and fusing it in a platinum crucible. Tungstate of potassa is thus formed, which is dissolved in hot water, with half its weight of muriate of ammonia, evaporated to dryness, and heated red hot in a Hessian crucible. The mass is then well washed with boiling water, and digested in weak solution of potassa. The residue is oxide of tungsten. In this process the tungstate of potassa and muriate of ammonia form chloride of potassium and tungstate of ammonia; but at a red heat the ammonia decomposes the tungstic acid, and reduces it to the state of oxide, which is prevented by the fused chloride of potassium from passing into the state of acid. (Wöhler, *Quarterly Journal*, xx. 177.) Thus prepared, the oxide is black, and when heated to redness, it suddenly ignites, and becomes converted into tungstic acid by the absorption of oxygen. It does not appear capable of entering into combination with the acids so as to form salts. When a current of hydrogen gas is carefully passed over heated tungstic acid, it is partially deoxydized and converted into a chocolate-coloured oxide, which neither combines with acids nor with bases, and which is identical in composition with the above. (*Ann. de Chim. et Phys.* xvii. 16.) If the action of hydrogen be too long continued, the oxide itself is reduced.

Tungstic Acid is obtained when the oxide is heated red-hot and stirred, in an open vessel. When finely powdered native tungstate of lime is boiled for some hours in nitric acid, tungstic acid is separated in the form of a yellow powder, which may be freed from adhering nitric acid, by dissolving it in ammonia, and heating the tungstate of ammonia to redness. Tungstate of potassa, prepared by heating wolfram with carbonate of potassa, as above described, may also be decomposed by nitric acid, and the precipitate heated with ammonia as before.

Tungstic acid is a yellowish powder, which appears green whilst hot, and also acquires a greenish colour by long exposure to the sun's rays. Its specific gravity is 6.12. It is insoluble in water, but readily soluble in the caustic alkalis. When precipitated by the acids from its ammoniacal solution, a portion of the precipitant is carried down with it.

When metallic zinc is put into a mixture of muriatic and tungstic acids, or when tungstate of ammonia is decomposed by distillation in a retort, a blue powder is obtained, which has sometimes been regarded as a distinct oxide, but which, according to Berzelius, is a tungstate of the oxide, or a compound of the acid and oxide.

Some of the tungstates have been examined by Scheele, and others by Vauquelin and Hecht (*Journal des Mines*, No. 19), but their history remains very imperfect.

Tungstate of Ammonia is procured in crystalline scales, of a metallic taste, by digesting the acid in ammonia or its carbonate. It contains, according to Vauquelin, 78 of acid, and 22 ammonia and water.

Tungstate of Potassa is uncrystallizable and deliquescent. The acids occasion precipitates in its solution, which are triple compounds of tungstic acid, potassa, and the acid used as precipitant. The *Nitrotungstate of Potassa* is the salt originally described by Scheele as tungstic acid. It dissolves in 20 parts of water, at 212°, and reddens litmus.

Tungstate of Soda crystallizes in hexaëdral tables, soluble in 4 of cold, and 2 parts of boiling water, and of an acrid taste. Sulphuric, nitric, and muriatic acids occasion precipitates, as in the tungstate of potassa.

Tungstate of Lime, of Baryta, and of Strontia, are insoluble white compounds.

Tungstate of Magnesia is obtained by boiling the acid with magnesia, filtering, and evaporating; it crystallizes in pearly scales. The acids produce precipitates of triple compounds in its solution.

Tungstate of Manganese, formed by adding tungstate of potassa to muriate of manganese, is an insoluble white powder. (John, *Gehlen's Journal*, iv.) *Tungstate of Iron* is also insoluble: *Tungstate of Zinc* and of *Tin* have not been examined, nor have any of the remaining tungstates been examined in their pure state.

Chlorides of Tungsten.—Wöhler has described two compounds of chlorine of tungsten. The *perchloride* is obtained by heating the oxide in chlorine; a white crystalline sublimate is produced, extremely volatile, and converted by water into tungstic and muriatic acids: it consists of

1	proportional of tungsten	=	296
3	„	chlorine (36 × 3)	.	.	.	=	108
							<hr/>
							214

The *protochloride* forms red acicular crystals, is fusible, and converted by water into oxide of tungstic and muriatic acid. Potassa dissolves it, with the disengagement of hydrogen gas, and chloride of potassium and tungstate of potassa are the results. It is, strictly speaking, a deutochloride, composed of

1	proportional of tungsten	=	96
2	„	chlorine (36 × 2)	.	.	.	=	72
							<hr/>
							168

Fluoride of Tungsten was procured by Berzelius, by evaporating a solution of tungstic acid in hydrofluoric acid to dryness.

Sulphuret of Tungsten is formed by heating 1 part of tungstic acid mixed with 4 of sulphuret of mercury. The mercury is expelled, and a dark gray compound, resembling sulphuret of copper, remains, consisting of

Tungsten	74.891
Sulphur	25.109
							<hr/>
							100.

This result indicates 1 proportional of tungsten = 96 + 2 proportionals of sulphur = 32. It is, therefore, a *bisulphuret of tungsten*. (Berzelius.)

The remaining compounds of tungsten have scarcely been investigated, and appear of little interest or importance.

Section XXVI. COLUMBIUM.

THIS metal was discovered in 1801 by Mr. Hatchett, in a mineral from North America. It was afterwards found combined with the oxides of iron and manganese, and also with yttria, in the Swedish minerals called *tantalite* and *yttrio-tantalite*.

Tantalite is chiefly found in octoëdral crystals, and in masses of a black or gray colour, in Finland. Its specific gravity is 7.9, and it contains, according to Ekeberg,

80	oxide of columbium
12	oxide of iron
8	oxide of manganese.

Yttero-tantalite is found at Ytterby, in Sweden. It contains about 45 per cent. of oxide of columbium. Its colour is dark gray, its lustre shining, and somewhat metallic.

Columbium was discovered in these minerals by M. Ekeberg, and, considering it as a *new* metal, he called it *tantalum*. In 1809 (*Phil. Trans.*) Dr. Wollaston examined these and the original mineral in the British Museum, and demonstrated the identity of columbium and tantalum. As the former name was given to this body by its original discoverer, it is here retained.

Columbium may be procured from columbite or tantalite, by the following process:—Mix 5 parts of the finely powdered mineral with 25 of carbonate of potassa, and 10 of borax; fuse the mixture, and when cold, digest it in muriatic acid; this dissolves every thing except the peroxide of columbium, which remains in the form of a white powder (Wollaston, *Phil. Trans.* 1809, p. 248). From 5 grains of columbite, Dr. Wollaston obtained

Oxide of columbium	.	.	.	4 grains
„ iron	.	.	.	$\frac{3}{4}$
„ manganese	.	.	.	$\frac{1}{4}$

From 5 grains of tantalite he procured

Oxide of columbium	.	.	.	$4\frac{1}{4}$ grains
„ iron	.	.	.	$\frac{1}{2}$
„ manganese	.	.	.	$\frac{2}{10}$

Berzelius is the only person who has obtained metallic columbium: he procured it by heating potassium with the potasso-fluoride of columbium, and washing the reduced mass with water. He describes it as having the colour of iron, very hard and brittle, and burning at a red heat into a whitish oxide. Its specific gravity is about 6. It is insoluble in muriatic, nitric, and nitro-muriatic acids. Heated to redness, it burns with a feeble flame. Mixed with nitre, and projected into a red-hot crucible, it detonates, and is oxidized. It forms alloys with other metals. (*Ann. de Chim. et Phys.* iii. 140.)

The characters of white or peroxide of columbium are very well marked. It is nearly insoluble in muriatic, nitric, and sulphuric acids; it is very soluble in potassa, and carbonate of potassa; 8 grains of the latter, fused with 1 of the oxide, render it soluble in water. It is much less soluble in soda, and

only retained while hot. From the readiness with which this oxide combines with potassa, Mr. Hatchett called it *columbic acid*.

Columbate of Potassa, as appears from Mr. Hatchett's experiments, forms white glittering scales, like boracic acid. Acids precipitate the columbic acid from this solution.

Infusion of galls, added to the solution of columbate of potassa, produces a very characteristic orange-coloured precipitate. Neither ferrocyanate of potassa nor hydrosulphurets occasion any change.

There is, according to Wollaston, a character very peculiar to the peroxide of columbium, which is its ready solubility in tartaric, citric, and oxalic acids. In all these cases the *newly precipitated oxide* must be used; for, when dried, it becomes very intractable.

When columbic acid is intensely heated with charcoal, air being excluded, it is partly reduced and partly converted into a dark brown powder, which appears to be an oxide of columbium: it does not dissolve in the acids, but is readily converted into columbic acid by fusion with hydrate of potassa.

According to Berzelius, the oxygen in the oxide is to that in the acid in the ratio of 2 to 3, and the equivalent of columbium deduced from his experiments is 185. The oxide, therefore, will consist of

1 proportional of columbium	.	.	.	= 185
2 proportionals of oxygen (8×2)	.	.	.	= 16
				<hr/>
				201

and the acid of

1 proportion of columbium	.	.	.	= 185
3 proportionals of oxygen (8×3)	.	.	.	= 24
				<hr/>
				209

Chloride of Columbium.—When the metal is heated in chlorine, a white pulverulent compound is produced, which, by the action of water, is converted into columbic and muriatic acids.

Nothing is known of the *iodide* or *bromide* of columbium; but the *fluoride* has been described by Berzelius.

Sulphuret of Columbium is formed by passing the vapour of sulphuret of carbon over columbic acid, heated to whiteness in a porcelain tube.

Section XXVII. NICKEL.

NICKEL is found native; combined with arsenic; and with arsenic acid. It is procured pure by the following process:—Dissolve the impure metal, sold under the name of *Speiss*, in sulphuric acid, by adding the quantity of nitric acid necessary to produce the solution. Concentrate this solution, and set it aside; fine green crystals of sulphate of nickel make their appearance. — Proceed in this manner till you have obtained a sufficient quantity of crystals. Dissolve them in water, and crystallize a second time. If they be now dissolved in water, and decomposed by an alkali, pure oxide of nickel will fall. Mix it with 3 *per cent.* of resin, make it into a paste with oil, and expose it to the most violent heat of a forge, in a charcoal crucible. A button of pure nickel will be obtained. (Thomson's *System*.)

The following is Mr. Mills's process for obtaining pure Nickel. (*Ann. of Phil.* iii. 210.)

Let the native arseniuret or sulphuret of nickel be finely pounded, and mixed with charcoal, also pounded, and placed in a flat-bottomed crucible, and exposed to a dull red heat for two hours; blow off the charcoal with a pair of bellows, and dissolve the nickel in nitro-sulphuric acid; evaporate and crystallize: beautiful green crystals, in the form of a square solid, will be obtained. Let these be carefully selected, dissolved in water, recrystallized, and mixed with a small portion of borax and pounded charcoal, and fused for a quarter of an hour in a strong red heat: when cold break the crucible, and underneath the borax will be found a button of nickel.

If the most perfect crystals of sulphate of nickel, obtained by either of the above processes, be very carefully selected, and purified by a second solution and crystallization, they are sometimes nearly pure, but it is extremely difficult to obtain them perfectly free from copper, cobalt, and even arsenic. This may, perhaps, be best effected by dissolving them in water slightly acidulated by sulphuric acid, and passing sulphuretted hydrogen through the solution: copper and arsenic are thus precipitated, and the liquid, after having been heated

to expel sulphuretted hydrogen, may be precipitated by carbonate of potassa, which separates from it the hydrated oxides of nickel and cobalt: these having been well washed, may be diffused in water, and chlorine passed through the mixture: a solution of muriate of nickel is thus obtained, and the cobalt thrown down in the form of an insoluble black peroxide, separable by filtration. From the muriatic solution, a carbonate of nickel may be precipitated by carbonate of potassa, which may be used as a source of the pure metal, or its salts. Or, the oxides of cobalt and nickel may be separated by the action of potassa on their ammoniacal solution, as described in the section on Cobalt.

Nickel is a white metal, which acts upon the magnetic needle, and is itself capable of becoming a magnet. It is difficultly fusible, but absorbs oxygen readily when heated red hot. It is malleable, and its specific gravity is about 8.5.

Protoxide of Nickel is obtained by adding potassa to the solution of the pure nitrate or sulphate; a precipitate falls of a pale green colour, which is a *hydrate*, or compound of oxide of nickel with water; this, heated to redness, affords a gray oxide, consisting, according to Tuputi (*Ann. de Chim.*, lxxx.) of 100 metal + 27 oxygen.

The carbonate, or nitrate of nickel, heated to redness, also afford the protoxide in the form of a gray powder.

The equivalent of the metal nickel is 28, and the protoxide, which is the only salifiable oxide, consists of

1	proportional of nickel	=	28
1	„ oxygen	=	8
									<hr/>
									36

This oxide easily dissolves in ammonia, forming a sapphire-blue solution; this property is often made use of to separate oxides of nickel and iron, the latter being insoluble in ammonia.

According to Thenard, if chlorine be passed through a mixture of the hydrate of nickel and water, a black *peroxide* is formed, which, when acted upon by the acids, evolves oxygen, and returns to the state of protoxide. This only happens, however, when the chlorine is in considerable excess; otherwise, a green solution of muriate of nickel is obtained.

Chloride of Nickel.—When nickel is heated in chlorine a *chloride* results. This compound may also be obtained by heating muriate of nickel to redness in a glass tube; a yellow scaly body is obtained, consisting of

1	proportional of nickel	= 28
1	„	chlorine	= 36
							<hr/> 64

Muriate of Nickel, formed by dissolving the oxide or carbonate of nickel in muriatic acid, is obtained by evaporation in a confusedly crystalline mass, of an apple-green colour and sweetish taste: it is soluble in about 2 parts of water at 60°.

Ammonio-muriate of Nickel is a green crystallizable salt.

Chlorate of Nickel.—Not examined.

Iodide of Nickel may be formed by adding solution of hydriodate of potassa to sulphate or nitrate of nickel; it is of a greenish-yellow colour, and insoluble.

Iodate of Nickel has not been examined.

The *bromide* and *fluoride* of nickel have not been examined.

Nitrate of Nickel is a green deliquescent salt, difficultly crystallizable in rhomboids. The analyses of this salt are much at variance, but it probably consists of

1	proportional of oxide of nickel	= 36
1	„	nitric acid	= 54
							<hr/> 90

The crystals contain 3 proportionals of water; or 5, according to Thomson (*First Lines*, ii. 334); they are soluble in 2 parts of water at 60°, and also dissolve in alcohol.

By adding excess of ammonia to nitrate of nickel, and evaporating, green crystals of *ammonio-nitrate of nickel* are obtained, the solution of which affords no precipitate with potassa or soda.

Sulphurett of Nickel may be formed by fusion. It is a brittle yellow compound, consisting of

1	proportional of nickel	= 28
1	„	sulphur	= 16
							<hr/> 44

When sulphuretted hydrogen is passed into a neutral solution of nickel, a great part of the metal falls in the form of a

black sulphuret or hydrosulphuretted oxide; if the solution be acid, the metal is not thus precipitated: hence the method of separating nickel from certain other metals, the precipitation of which is not prevented by excess of acid.

Neither the *Hyposulphite* nor the *Sulphite of Nickel* have been examined.

Sulphate of Nickel is formed by digesting the oxide or carbonate in dilute sulphuric acid. A bright green solution is formed, which affords quadrangular prismatic crystals, soluble in about 3 parts of water at 60° , and which effloresce by exposure. Their taste is sweet and astringent. Exposed to heat, they crumble down into a yellow powder. This salt is also obtained by heating common nickel in sulphuric acid, with the occasional addition of nitric acid; though it is seldom pure when thus prepared.

The crystallized sulphate of nickel contains 7 proportionals of water, and is composed as follows:—

1 proportional of oxide	=	36
1 „ acid	=	40
7 proportionals of water (9×7)	=	63
						<hr/>
						139

Sulphate of Ammonia and Nickel is formed by evaporating a mixed solution of ammonia, and sulphate of nickel; it forms four-sided prismatic crystals. It consists of

1	proportional of sulphate of ammonia	.	.	.	=	57
1	„ sulphate of nickel	.	.	.	=	76
7	proportionals of water (9×7)	.	.	.	=	63
						<hr/>
						196

Sulphate of Potassa and Nickel is obtained by adding potassa to sulphate of nickel (not in excess), filtering and evaporating. It forms green rhomboidal crystals, of a sweetish and bitter taste, consisting, according to Mr. Cooper, (*Ann. of Phil.* vi. 440,) of

Sulphuric acid	37.90
Oxide of nickel	17.54
Potassa	20.48
Water	24.08
					<hr/>
					100.

or, according to Dr. Thomson, (*First Principles*, ii. 435) of

1 proportional of sulphate of potassa	.	.	.	=	88
1 " sulphate of nickel	.	.	.	=	76
6 proportionals of water (9×6)	.	.	.	=	54
					<hr/>
					218

Sulphate of Nickel and Iron is formed by dissolving the mixed protoxides in sulphuric acid. It is a green efflorescent salt, in tabular crystals.

Phosphuret of Nickel is a brittle whitish compound, decomposed by exposure to heat and air.

Hypophosphite and Phosphite of Nickel remain unexamined.

Phosphate of Nickel, being nearly insoluble, is precipitated upon adding phosphate of soda to a solution of nickel. It is of a pale green colour. Digested in phosphate of ammonia, a triple ammonio-phosphate of nickel is formed: it is insoluble in water.

Carburet of Nickel occasionally remains in the form of a shining powder, when a button of the metal, which has long been fused in the contact of carbon, is dissolved in nitric acid.

Carbonate of Nickel is precipitated in the form of a green powder, when carbonate of potassa is added to sulphate of nickel. It is probably a compound of

1 proportional of oxide of nickel	=	36
1 " carbonic acid	=	22
					<hr/>	58

Dried in the air at the temperature of 60° , it retains, according to Thomson, 3 proportionals of water. It dissolves in excess of carbonic acid.

Ammonio-carbonate of Nickel is a very soluble and difficultly crystallizable salt. If its solution be heated, carbonic acid and ammonia are evolved, and hydrated oxide of nickel is thrown down.

Borate of Nickel is a pale green insoluble compound.

Ferrocyanate of Potassa occasions a very characteristic pale gray precipitate in dilute solutions of nickel: in concentrated solutions the precipitate is pale green.

Arseniate of potassa, dropped into nitrate of nickel, occasions the precipitation of a pale green *arseniate of nickel*.

The Salts of Nickel are distinguished by the fine green colour of their solutions, and by affording a green precipitate with

ammonia, soluble in excess of that alkali, when it assumes a blue colour. The yellow-green precipitate afforded by hydriodate of potassa is very characteristic of nickel; but the nicest test of its presence is the ferrocyanate of potassa, which produces a pale gray or greenish white precipitate in all the solutions of the metal. To detect the presence of nickel in iron, Dr. Wollaston recommends that a small portion, which need not exceed .01 of a grain, should be filed from the sample, and dissolved in a drop of nitric acid; evaporate this to dryness, and add a drop or two of liquid ammonia, which, when gently warmed, will dissolve any oxide of nickel that may be present. The transparent part of the fluid is then to be conducted by the end of a glass rod to a small distance from the precipitated oxide of iron, and mixed with a drop of ferrocyanate of potassa, which, if nickel be present, will cause an immediate milkiness, not discernible in a solution of common iron, formed and treated in the same way.

Of the *Alloys of Nickel* there is one which requires particular notice, namely, that with iron, which forms the principal metallic ingredient in those lapideous masses, which, in different countries, have fallen upon our globe, and which have been termed *aërolites*, or *meteoric stones*. Though we really know nothing of the source or origin of these bodies, it has been ascertained upon the most satisfactory and indisputable evidence, that they are not of terrestrial formation; and, consequently, since men began to think and reason correctly, their visits to our planet have awakened much speculation, and some experimental research.

In the first place, it deserves to be remarked, that we have very distinct evidence of the falling of stony bodies from the atmosphere in various countries, and at very remote periods. For, to say nothing of the fabulous narrations which encumber the annals of ancient Rome, or the extended catalogue of wonders flowing from the lively imagination of oriental writers, such events are recorded in holy writ, and have been set down by the most accredited of the early historians; and although philosophic scepticism long contended against the admission of the fact, it has in modern times received such unanswerable proofs, as to be allowed by all who have candidly considered the evidence, and is only rejected by the really ignorant, or by those who, for the sake of singularity, affect disbelief.

The first tolerably accurate narration of the fall of a meteoric stone relates to that of Ensisheim, near Basle, upon the Rhine. The account which is deposited in the church runs thus : A.D. 1492, Wednesday, 7 November, there was a loud clap of thunder, and a child saw a stone fall from heaven : it struck into a field of wheat, and did no harm, but made a hole there. The noise it made was heard at Lucerne, Tilling, and other places ; on the Monday King Maximilian ordered the stone to be brought to the castle, and after having conversed about it with the noblemen, said the people of Ensisheim should hang it up in their church, and his Royal Excellency strictly forbade anybody to take anything from it. His Excellency, however, took two pieces himself, and sent another to Duke Sigismund of Austria. This stone weighed 255 lbs.

In 1627, 27th November, the celebrated Gassendi saw a burning stone fall on Mount Vaisir, in Provence : he found it to weigh 59 lbs.

In 1672, a stone fell near Verona, weighing 300lbs. And Lucas, when at Larissa, in 1706, describes the falling of a stone, with a loud hissing noise, and smelling of sulphur.

In September, 1753, de Lalande witnessed this extraordinary phenomena near Pont de Vesle. In 1768, no less than three stones fell in different parts of France. In 1790, there was a shower of stones near Agen, witnessed by M. Darcet, and several other respectable persons. And on the 18th of December, 1795, a stone fell near Major Topham's house, in Yorkshire ; it was seen by a ploughman and two other persons, who immediately dug it out of the hole it had buried itself in ; it weighed 56 lbs.*

We have various other and equally satisfactory accounts of the same kind. All concur in describing a luminous meteor, moving through the air in a more or less oblique direction, attended by a hissing noise, and the fall of stony or semi-metallic masses, in a state of ignition. We have, however, evidence of another kind, amply proving the peculiarities of these bodies. It is, that although they have fallen in very different countries, and at distant periods, when submitted to chemical

* In Ure's Chemical Dictionary there is a full chronological list of meteoric stones. (Art. METEOROLITE.)

analysis, they all agree in component parts; the metallic particles being composed chiefly of nickel and iron; the earthy of silica and magnesia.

Large masses of *native iron* have been found in different parts of the world, of the history and origin of which nothing very accurate is known. Such are the great block of iron at Elbogen, in Bohemia; the large mass discovered by Pallas, weighing 1600 lbs., near Krasnorjark, in Siberia; that found by Goldberry, in the great desert of Zahra, in Africa; probably, also, that mentioned by Mr. Barrow, on the banks of the great fish river in Southern Africa; and those noticed by Celis, Bruce, Bougainville, Humboldt, and others in America, of enormous magnitude, exceeding 30 tons in weight. That these should be of the same source as the other meteoric stones, seems at first to startle belief; but when they are submitted to analysis, and the iron they contain found alloyed with nickel, it no longer seems credulous to regard them as of meteoric origin. We find nothing of the kind in the earth.

To account for these uncommon visitations of metallic and lapideous bodies, a variety of hypotheses have been suggested.

Are they merely earthly matter, fused by lightning? Are they the offspring of any terrestrial volcano? These were once favourite notions; but we know of no instance in which similar bodies have in that way been produced, nor do the lavas of known volcanos in the least resemble these bodies; to say nothing of the inexplicable projectile force that would here be wanted. This is merely explaining what is puzzling, by assuming what is impossible; and the persons who have taken up this conjecture, have assumed one impossibility to account for what they conceive to be another, namely, that the stony bodies should come from any other source than our own globe.

The notion that these bodies come from the moon, is, when impartially considered, neither absurd nor impossible. It is quite true, that the quiet way in which they visit us is against such an origin; it seems, however, that any power which would move a body 6000 feet in a second, that is, about three times the velocity of a cannon-ball, would throw it from the sphere of the moon's attraction into that of our earth. The cause of this projective force may be a volcano, and if thus impelled, the body would reach us in about two days, and enter

our atmosphere with a velocity of about 25,000 feet in a second. Their ignition may be accounted for, either by supposing the heat generated by their motion in our atmosphere sufficient to ignite them, or by considering them as combustibles, ignited by the mere contact of air.

While we are considering the *possibility* of these opinions, it may be remembered, that in the great laboratory of the atmosphere, chemical changes *may* happen, attended by the *production* of iron and other metals; that, at all events, such a circumstance is within the range of possible occurrences; and that the meteoric bodies which thus salute the earth with stony showers, may be children of the air, created by the union of simpler forms of matter. The singular relationship between iron and nickel, and magnetism, and the uniform influence of meteoric phenomena on the magnetic needle, should be taken into account in these hypotheses.

Meteoric stones have generally an uneven black surface, and are internally of a gray colour and coarse texture. When carefully examined, they appear made up of a number of small spherical bodies and metallic grains imbedded in a softer matter, composed, according to Mr. Howard (*Phil. Trans.*, 1802), of silica, magnesia, and iron with a little nickel; the spherical bodies are nearly of similar composition; and the metallic grains are partly *meteoric iron*, and partly the same with a little sulphur. In addition to these substances, Vauquelin found 2 *per cent.* of chrome in a stone which fell at Langres, in 1815. (*Ann. de Chim. et Phys.*, i. 53.) And Stromeyer detected cobalt in the meteoric iron from the Cape of Good Hope. (Thomson's *Annals*, ix.) Lime and alumine have also been found in them, and a small proportion of manganese. M. Laugier has lately announced the existence of a meteoric stone without nickel, but containing chrome; and as he has detected the latter metal in all the *aërolites* which he has examined, he considers it as their most characteristic ingredient.—*Mem. du Museum*, vi. p. 233.

In meteoric iron the proportion of nickel varies considerably. In a specimen from the Arctic region I found 3.2 *per cent.* (*Quarterly Journal*, vi. 369.) In that from Siberia, Mr. Children found nearly 10 *per cent.* The analysis may be performed by solution in nitro-muriatic acid; the iron is

thrown down by excess of ammonia in the state of peroxide, of which 100 grains indicate 70 of metallic iron; it is separated by filtration, washed and dried, and on evaporating the filtrated liquor and heating its dry residue red-hot, the oxide of nickel is obtained, which should be redissolved in nitric acid, and precipitated by pure potassa, the mixture being boiled for a few seconds. 100 grains of this oxide of nickel are equal to 79 of metallic nickel.—Children, *Quarterly Journal*, ix. 324.

Meteoric iron has been imitated by fusing iron with nickel. The alloy of 90 iron with 10 nickel is of a whitish-yellow cast, and not so malleable as pure iron. The alloy with 3 *per cent.* of nickel is perfectly malleable and whiter than iron. These alloys are less disposed to rust than pure iron, but nickel alloyed with steel increases the tendency to rust. — Stodart and Faraday, *Quarterly Journal of Science and Arts*, ix.

The remaining alloys of nickel have been little examined. Nothing is known of its compounds with potassium, sodium, manganese, zinc, or tin. With copper it forms a hard white alloy; the *white copper* of the Chinese consists, according to the analysis of Dr. Fyfe, of

40.4	parts of copper
31.6	„ nickel
25.4	„ zinc
2.6	„ iron
<hr/>	
100.	

Its other alloys have not been examined.

Section XXVIII. MERCURY.

THE principal ore of this metal is the sulphuret, or *native cinabar*, from which the mercury is separated by distillation with quicklime or iron filings.

Mercury is a brilliant white metal, having much of the colour of silver, whence the terms *hydrargyrum*, *argentum vivum*, and *quicksilver*. It has been known from very remote

ages. It is liquid at all common temperatures; solid and malleable at -40° , and contracts considerably at the moment of congelation; its specific gravity in the frozen state being 15.6. It boils and becomes vapour at about 670° . Its specific gravity at 60° is 13.5.

Mercury is sometimes adulterated with the alloy of lead and bismuth, a fraud easily detected by the want of its due fluidity, and by its not being perfectly volatile, but leaving a residuum when boiled in a platinum or iron spoon. The best method of purifying mercury is to redistil it in an iron retort.

Native Mercury occurs in small fluid globules, in most of the mines producing the ores of this metal.

Mercury and Oxygen.—There are two oxides of mercury. The *black*, or *protoxide*, was formerly obtained by long agitation of the metal in contact with oxygen. It is insipid, and insoluble in water, and was called in old pharmacy, *Ethiops per se*.

The simplest process for its preparation consists in decomposing the protochloride of mercury by excess of solution of potassa, washing the product with cold water, and drying it at common temperature in a dark place. If heated or exposed to the sun's rays, it is resolved into peroxide and metallic mercury. A preparation nearly corresponding with this oxide is directed in the *London Pharmacopæia*, under the name of *Hydrargyri oxidum cinereum*; it is also contained in the *Pilula hydrargyri*, or *blue pill*, and in the *unguentum hydrargyri*. Some have regarded these preparations as merely containing *finely-divided* mercury, and deny the possibility of oxydizing the metal when pure by mere agitation in the contact of atmospheric air, and it is certain that perfectly pure mercury, if at all thus acted on, is converted into an oxide extremely slowly, whilst mercury, containing a little lead or bismuth, is speedily converted into a black powder.

The *red* or *peroxide* of mercury is produced by exposing the metal, heated nearly to its boiling point, to the action of air. It becomes coated with reddish-brown scales, spangles, and crystals, and is ultimately entirely converted into a red shining mass, called in old pharmaceutical works, *precipitatum per se* or *calcined mercury*. It is the *hydrargyri oxydum rubrum* of the present *London Pharmacopæia*. It is most easily obtained

by introducing into a flat-bottomed matrass, of the annexed shape, about 4 ounces of mercury, and placing it in a sand bath, heated nearly to the boiling point of the metal. In about a month's time nearly the whole is converted into oxide. Air is freely admitted by the tube, while its length prevents the escape of mercurial vapour, which condenses and falls back into the body of the vessel; the remaining portion of running mercury may be driven off by exposing it in a basin to a heat just below redness.



Peroxide of mercury has an acrid metallic taste, and is poisonous; it dissolves very sparingly in water. When heated, it acquires a black colour, but becomes again red on cooling; at a red heat it evolves oxygen, and is reduced to the metallic state. It should be entirely volatilized when placed upon a red-hot iron, for it is sometimes adulterated with red lead.

The oxygen in the protoxide of mercury is to that in the peroxide in the ratio of 1 to 2; and assuming the number 200 as the equivalent of mercury, the protoxide will consist of

1	proportional of mercury	.	.	.	=	200
1	„ oxygen	.	.	.	=	8
						<hr/>
	Equivalent of protoxide of mercury	.			=	208

And the peroxide, of

1	proportional of mercury	.	.	.	=	200
2	„ oxygen (8 × 2)	.	.	.	=	16
						<hr/>
	Equivalent of the peroxide of mercury	.			=	216

Both these oxides combine with the greater number of the acids forming distinct salts, several of which are resolvable into salts with excess of base, and salts with excess of acid, so that the history of the saline combinations of mercury is thus rendered somewhat complex.

Mercury and Chlorine combine in 2 proportions, and a protochloride and perchloride of mercury are the results. These compounds are usually called *calomel* and *corrosive sublimate*. In the *London Pharmacopæia* they have received the improper

names of *submuriate of mercury* and *oxymuriate of mercury*. The protochloride consists of

1	proportional of mercury	.	.	.	=	200
1	„ chlorine	.	.	.	=	36
						<hr/>
	Equivalent of protochloride of mercury	.			=	236

And the perchloride, of

1	proportional of mercury	.	.	.	=	200
2	proportionals of chlorine (36×2)	.	.	.	=	72
						<hr/>
	Equivalent of the perchloride of mercury				=	272

Protochloride of Mercury.—This compound, commonly termed *calomel*, is first mentioned by Crolius, early in the seventeenth century. The first directions for its preparation are given by Beguin, in the *Tyrocinium Chemicum*, published in 1608. He calls it *draco mitigatus*. Several other fanciful names have been applied to it, such as *aquia mitigata*, *manna metallorum*, *panchymagogum minerale*, *sublimatum dulce*, *mercurius dulcis*, &c.

The most usual mode of preparing calomel consists in triturating two parts of corrosive sublimate with one of mercury, until the globules disappear, and the whole assumes the appearance of an homogeneous gray powder, which is introduced into a matrass, placed in a sand heat, and gradually raised to redness. The calomel sublimes, mixed with a little corrosive sublimate, the greater part of which, however, being more volatile than the calomel, rises higher in the matrass; that which adheres to the calomel may be separated, by reducing the whole to a fine powder, and washing in large quantities of hot distilled water. Pure calomel, in the form of a yellowish white insipid powder, remains.

It was formerly the custom to submit calomel to very numerous sublimations, under the idea of rendering it *mild*; but these often tended to the production of corrosive sublimate; and the calomel of the first sublimation, especially if a little excess of mercury be found in it, is often more pure than that afforded by subsequent operations.

The following are the directions given in the *London Pharmacopœia* for 1809, for the preparation of calomel, upon the above principle:—

“Take of oxymuriate of mercury, 1 lb.

„ purified mercury, *by weight*, 9 oz.

Rub them together, until the metallic globules disappear; then sublime: take out the sublimed mass, reduce it to powder, and sublime it in the same manner twice more successively. Lastly, bring it to the state of a very fine powder; throw this into a large vessel, full of water; then stir it, and, after a short interval, pour the supernatant turbid solution into another vessel, and set it by, that the powder may subside. Lastly, having poured away the water, dry the powder.”—Powell's *Translation of the London Pharmacopœia*, Lond. 1815, p. 144 and 99.

It will be observed, that in these processes the operation consists in reducing the perchloride to the state of protochloride by the addition of mercury. Various modes have, however, been adopted for the direct formation of calomel: two of these may here be noticed, of which the first is in the humid way, as devised by Scheele and Chenevix. It is as follows:

Form a nitrate of mercury, by dissolving as much mercury as possible in hot nitric acid; then dissolve in boiling water a quantity of common salt, equal to half the weight of the mercury used, and render the solution sensibly sour by muriatic acid, and pour the hot nitrate of mercury into it. Wash and dry the precipitate.

If this process be carefully performed, and the precipitate thoroughlyedulcorated, the calomel is said to be sufficiently pure, but I should not recommend it for pharmaceutical use.

The second process, however, or that by which calomel is directly formed in the dry way, appears, on the whole, the least exceptionable for the production of this very important article of pharmacy; it is the method followed at Apothecaries' Hall, sanction having been obtained for its adoption from the College of Physicians, and it has been introduced into the last edition of the *Pharmacopœia*. The process there directed is as follows:—

“Take of purified mercury, *by weight* four pounds,

„ sulphuric acid, *by weight*, thirty ounces,

„ muriate of soda, a pound and a half,

„ muriate of ammonia, eight ounces;

Boil two pounds of the mercury with the sulphuric acid in a glass vessel, until the sulphate of mercury is dry. When it

has cooled, rub it with two pounds of the mercury in an earthenware mortar, till they are well mixed. Then add the muriate of soda, and rub them together until globules are no longer visible. Then sublime. Reduce the sublimate to a very fine powder, pass it through a sieve, and mix it well with the muriate of ammonia previously dissolved in a gallon of distilled water. Set it by, that the powder may subside. Pour off the liquor and wash the powder frequently with boiling distilled water, until solution of ammonia, dropped in, produces no precipitate. Lastly, reduce it to a very fine powder in the manner we have directed for the preparation of chalk."

The following observations upon the above process I annex from my *Manual of Pharmacy* :—

This process for the preparation of calomel was originally adopted at Apothecaries' Hall, and has many advantages over the more usual method of the former pharmacopœia. A persulphate of mercury is first formed by boiling two pounds of the metal with thirty ounces of sulphuric acid to dryness. This process may be performed in the large way, in a cast-iron vessel, which should be conveniently arranged for the escape of the abundant fumes of sulphurous acid developed by the action of the mercury, and which are often a serious nuisance to the neighbourhood. They may be very effectually annihilated by suffering them to pass through a very long flue and lofty chimney, mixed with abundance of coal smoke. The *persulphate* of mercury is triturated with a sufficient quantity of metallic mercury to convert it into a *protosulphate*, and then mixed with a due proportion of common salt, and subjected to sublimation.

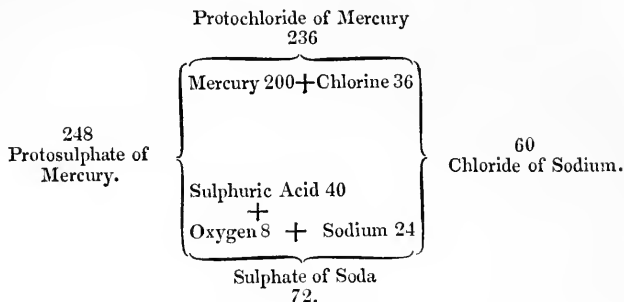
Protosulphate of mercury is a compound of

1	proportional of protoxide of mercury	.	=	208	83.8
1	„ sulphuric acid	.	=	40	16.2
				<hr/>	<hr/>
				248	100

To convert it into calomel it requires *one* proportional of chloride of sodium (common salt), the nature of the action of which, and the proportions of results, will be evident from the following Table, premising that calomel consists of

1	proportional of mercury	.	=	200	84.75
1	"	chlorine	.	=	36
				<hr/>	<hr/>
				236	100

It is, therefore, a *protochloride of mercury*.



In this decomposition (as in that for the formation of corrosive sublimate) the oxygen of the oxide of mercury (contained in the sulphate) is transferred to the *sodium* of the common salt, which thus becomes *soda*, and forms, with the sulphuric acid, a sulphate of soda.

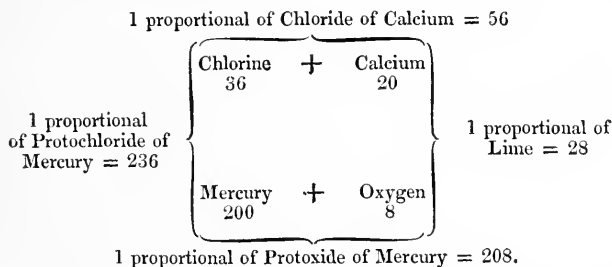
The further directions relate to the washing of the calomel in order to ensure the separation of any adhering corrosive sublimate, and to its reduction into the state of a very fine powder. In the elutriation, muriate of ammonia is employed in consequence of the extreme solubility which it confers on the perchloride of mercury: common salt answers equally well and is cheaper, but it deserves notice in relation to this part of the process, that calomel *boiled* with solution of sal-ammoniac, or of common salt, is resolved into metallic mercury and corrosive sublimate; the washings, therefore, should be with *cold* water, or with water not exceeding 80°, by which any such re-action is avoided. This important fact in regard to the purification of calomel was first pointed out to me by Mr. Hennel, of Apothecaries' Hall.

The form in which calomel sublimes depends upon the dimensions and temperature of the subliming vessels. In small vessels it generally condenses in a crystalline cake, the interior surface of which is often covered with beautiful quadrangular prismatic crystals, perfectly transparent, and of a texture somewhat elastic or horny: in this state it acquires, by the necessary rubbing into powder, a decidedly yellow or buff colour, more or less deep according to the degree of trituration which it has undergone. If, on the contrary, the

calomel be sublimed into a very capacious and cold receiver, it falls in an almost impalpable and perfectly white powder, which only requires due elutriation to fit it for use; it then remains perfectly colourless. By a very obvious and simple modification of the process, it may be suffered as it sublimes to fall into water, according to Mr. Jewell's patent; but no equivalent advantage results from such mode of conducting the operation.

I have thought it right to state the above circumstances, to account for the various appearances under which calomel occasionally presents itself in commerce: it may be added, that the buff aspect of this substance indicates the absence of corrosive sublimate; though it by no means follows as a consequence, that when snow-white it contains it. When the surface of massive sublimed calomel is scratched, it always exhibits a buff colour.

Calomel should be perfectly tasteless, inodorous, and insoluble in water*. Its specific gravity is 7.2. It is decomposed by the fixed alkalis and by ammonia, and protoxide of mercury is one of the results. The theory of this decomposition in the case where lime water is used, as opposed to that of corrosive sublimate under similar circumstances, is shown in the annexed diagram:—



Calomel, if not carefully washed, may, under some circumstances, contain a minute portion of corrosive sublimate; it may be detected by boiling it in pure water, and adding to the

* Calomel is sometimes stated to be soluble to a very small extent in water, but after very careful washing I have found that boiling water filtered through it is not in the least affected by solution of sulphuretted hydrogen, provided care be taken to avoid the mixture of any suspended calomel.

filtered and cold liquor a few drops of an aqueous and transparent solution of white of egg. A white cloud indicates the presence of the perchloride of mercury or corrosive sublimate. The mode of testing calomel for the presence of corrosive sublimate, by boiling it in a weak solution of muriate of ammonia, and then adding carbonate of potassa, is obviously fallacious, in consequence of the *production* of corrosive sublimate under such circumstances, already adverted to.

It cannot, I think, be denied that the best pharmaceutical term for protochloride of mercury is CALOMEL; it is short, open to no misconception, and is not, like the term *submuriate of mercury*, calculated to convey a very erroneous idea of the nature of the compound.

Native Chloride of Mercury, or *Mercurial Horn Ore*, has been found in Germany, France, and Spain, usually crystallized, and sometimes incrusting and massive.

Perchloride of Mercury, or *Corrosive Sublimate*, may be obtained by a variety of processes.

When mercury is heated in excess of chlorine, it burns with a pale flame; the gas is absorbed, and a white volatile substance rises, which is the perchloride.

It may also be obtained by dissolving peroxide of mercury in muriatic acid, evaporating to dryness, redissolving in water, and crystallizing.

The ordinary process for making corrosive sublimate consists in exposing a mixture of chloride of sodium (common salt) and persulphate of mercury, to heat in a proper subliming vessel.

The following are the official directions of the *London Pharmacopœia*, for the preparation of corrosive sublimate, there termed *oxymuriate of mercury* :—

- “ Take of purified mercury, by weight 2 lbs.
- „ sulphuric acid, by weight 30 oz.
- „ dried muriate of soda, 4 lbs.

Boil the mercury with the sulphuric acid in a glass vessel, until the sulphate of mercury is dry. Rub this, when it is cold, with the muriate of soda in an earthenware mortar; then sublime from a glass cucurbit, by heat gradually increased.

The first step in this process is the formation of a dry *persulphate of mercury*; that is, of a salt composed of sulphuric

acid and peroxide of mercury, and containing, in its perfect state,—

1 proportional of peroxide of mercury	.	=	216	.	73
2 proportionals of sulphuric acid	.	=	80	.	27
			296	100	

This persulphate is then thoroughly mixed with chloride of sodium (common salt), called in the above formula *muriate of soda*, which is composed of

1 proportional of sodium	.	.	=	24	.	40
1 „ chlorine	.	.	=	36	.	60
			60	100		

Upon the application of heat to this mixture, the original substances are decomposed, *perchloride of mercury* (oxymuriate of mercury) sublimes, and sulphate of soda is the residue. The object, then, of the operation is, to obtain a compound of *one* proportional of mercury and *two* of chlorine, which is effected by the mutual decomposition of *one* proportional of persulphate of mercury, = 296, and *two* proportionals of chloride of sodium, $60 \times 2 = 120$, as shown in the following table :—

		Perchloride of Mercury,				
		272				
296 Persulphate of Mercury.	{	Mercury	+	Chlorine		
		200		72		
				120 Chloride of Sodium.	{	
		Sulphuric Acid 80				
		+				
		Oxygen 16 + Sodium 48				
		Sulphate of Soda,				
		144.				

The results, therefore, are *two* proportionals of sulphate of soda, = 144, and *one* proportional of perchloride of mercury, = 272, consisting of

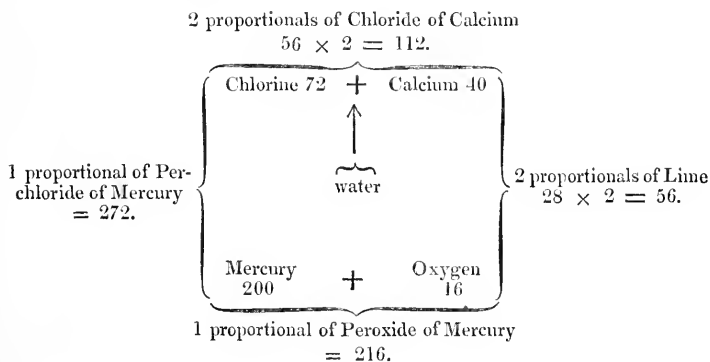
1 proportional of mercury	.	.	=	200	.	73.52
2 proportionals of chlorine (36×2)	.	.	=	72	.	26.48
				272	100.	

The persulphate of mercury is generally prepared upon the large scale, by heating the acid and metal in an iron pot, proper means being adopted to carry off the copious fumes of sulphurous acid arising from the decomposition of a portion of the sulphuric acid, during the peroxidizement of the mercury. The whole is then evaporated to dryness, and the subsequent sublimation is performed in glass, earthenware, or iron vessels, their form and arrangement being much dependent upon the quantity of materials employed.

As the only demonstrable components of perchloride of mercury are chlorine and mercury, the impropriety of the term "*hydrargyri oxyurias*," applied to it in the *Pharmacopœia*, is obvious; for it neither contains oxygen nor muriatic acid. To the erroneous views in which this term originated, it is not necessary now to allude; nor shall I recur to those masterly researches of Sir H. Davy, which first taught us to suspect their correctness, and afterwards completely exposed their fallacy: the compound before us ought obviously to be termed *perchloridum hydrargyri*; but, perhaps, as for pharmaceutical purposes it is often very inconvenient to adopt a correct philosophical nomenclature, the old term *hydrargyrum corrosivum sublimatum*, or CORROSIVE SUBLIMATE, would have been most prudently and conveniently retained.

Corrosive sublimate has an acrid nauseous taste, leaving a permanent metallic and astringent flavour upon the tongue. Its specific gravity is 5.2. It is usually met with in the shops in the form of white semitransparent and imperfectly crystallized masses, or in powder. It frequently exhibits prismatic crystals upon the inner surfaces of the sublimed cakes. It is soluble in 20 parts of water, at the temperature of 60°, and boiling water takes up about one-third its weight: alcohol at 60° dissolves half its weight, and ether, at the same temperature, about one-third its weight. When heated, it readily and entirely sublimes in the form of a dense white vapour, powerfully affecting the nose and mouth. It dissolves without decomposition in muriatic acid, but is insoluble in concentrated nitric and sulphuric acids. Muriatic acid of the specific gravity 1.158, at the temperature of 60°, dissolves about its own weight, and the solution when cooled to about 40°, concretes into a mass of acicular crystals.

When solutions of potassa, soda, or lime, are mixed with solution of corrosive sublimate, a yellow precipitate is thrown down, which is a hydrated peroxide of mercury. Such a mixture of a pint of lime-water with a drachm of corrosive sublimate was formerly much used as an application to venereal ulcers, under the name of "*aqua phagadænica*." It is in fact a solution containing undecomposed corrosive sublimate and chloride of calcium (muriate of lime) mixed with peroxide of mercury, *two* proportionals of lime being required for the decomposition of *one* proportional of corrosive sublimate, as shown in the following diagram, which also exhibits the theory of the decomposition:



When solution of corrosive sublimate is decomposed by ammonia, the result is not peroxide of mercury, but a white precipitate, which is composed of muriate of ammonia and peroxide of mercury.

Muriate of ammonia considerably increases the solubility of corrosive sublimate, one part rendering five parts soluble in rather less than five of water. Such solutions have occasionally been introduced into Pharmacopœiæ, and are useful for the internal exhibition of corrosive sublimate. Boerhaave's solution had a place in the Edinburgh Pharmacopœia of the year 1783; it was composed as follows:—

R Mercurii Sublimati Corrosivi gr. vj.
Salis Ammoniaci gr. xij. Solve in
Aquæ destillatæ libra una.

The solubility of corrosive sublimate is also much increased by common salt. A solution composed of 7 parts of salt and 20 of water dissolves 32 parts of corrosive sublimate: it deposits rhomboidal crystals, probably composed of one proportional of each of the chlorides. (J. Davy, *Phil. Trans.*, 1822, p. 364.)

Corrosive sublimate is decomposed by several of the metals: they generally abstract half the chlorine, and convert it into calomel.

When solution of ammonia is poured upon calomel, a black protoxide of mercury is formed; but ammonia, added to a solution of corrosive sublimate, occasions, as has just been remarked, a white precipitate of a *triple muriate of ammonia and mercury*.

A compound of this kind has long been used in pharmacy, under the name of *calx hydrargyri alba*, or *white precipitate*. It is the *hydrargyrum præcipitatum album* of the present *Pharmacopæia*, which directs the following process for its formation.

“ Take of oxymuriate mercury $\frac{1}{2}$ lb.
 „ muriate of ammonia 4 oz.
 „ solution of subcarbonate of potassa $\frac{1}{2}$ pint.
 „ distilled water 4 pints.

First dissolve the muriate of ammonia, then the oxymuriate of mercury, in the distilled water, and add thereto the solution of subcarbonate of potassa. Wash the precipitated powder until it becomes tasteless; then dry it.”

In this process a compound of muriate of ammonia and corrosive sublimate is decomposed by carbonate of potassa, carbonic acid is evolved, and a precipitate is formed, consisting of peroxide of mercury in combination with muriate of ammonia. The proportions, according to Mr. Hennell's experiments (*Quarterly Journal of Science*, vol. xviii. p. 297), are 80 peroxide of mercury + 20 muriate of ammonia, numbers which correspond with

1 proportional of peroxide of mercury	.	.	=	216
1 „ muriate of ammonia	.	.	=	54
Equivalent of white precipitate	.	.	=	270

This mercurial preparation is limited to external use. It is

sometimes employed, either alone, or mixed with a little powdered starch, for the destruction of vermin; this it effects without producing much cuticular irritation.

When a mixed solution of muriate of ammonia and bichloride of mercury is evaporated, the triple salt which is obtained was formerly called *sal alembroth*. The addition of potassa or soda to the solution throws down the above-mentioned white precipitate. When 34 parts of corrosive sublimate and 6.75 of muriate of ammonia are heated together in a glass tube, they form a compound more fusible and less volatile than either ingredient separate, which, on cooling, concretes into a gray translucent mass; when strongly heated, it suffers a partial decomposition.

Chlorate of Mercury.—Chloric acid dissolves both the oxides of mercury; the *protochlorate* has the appearance of a yellowish granular powder, sparingly soluble in hot water, and of a mercurial taste. The *perchlorate* forms white acicular crystals, having the acrid flavour of the perchloride, and soluble in 4 parts of water at 60°.—Vauquelin, *Annales de Chimie*, xcv.

Mercury and Iodine unite in two proportions. These compounds may be procured either by gently heating mercury with iodine, or by adding hydriodic acid to solutions of mercury. The *protiodide* is yellow, and is most readily obtained by adding a solution of iodide of potassium to one of protonitrate of mercury. When rapidly heated in a glass tube, it fuses, and sublimes unaltered. It consists of

1	proportional of mercury	=	200
1	„	iodide	=	125
								<hr/> 325

Periodide of Mercury is of a bright scarlet, and is precipitated by the addition of a solution of iodide of potassium to one of corrosive sublimate or of permnitrate of mercury: it is easily fusible, and assumes a yellow colour: it sublimes in rhomboidal scales, at first yellow, but becoming red on cooling. Acids and alcohol dissolve it by the aid of heat, and as the solutions cool, it separates in more or less perfect crystals; it dissolves also in solutions of the mercurial salts and of

iodide of potassium. It is precipitated by sulphuric acid from its solution in caustic potassa. It consists of

1	proportional of mercury	.	.	.	=	200
1	„	iodine (125 × 2)	.	.	=	250
					<hr/>	450

Iodate of Mercury.—Iodate of potassa occasions a white insoluble precipitate in protonitrate of mercury, but not in the pernitrate; hence the periodate appears to be a soluble salt.

Bromide of Mercury.—Bromide of potassium occasions a white curdy precipitate in the protonitrate of mercury, and a yellowish precipitate in the pernitrate, soluble in excess of acid.

The *Bromates of Mercury* have not been examined.

Fluorides of Mercury.—Hydrofluoric acid occasions no precipitate in the protonitrate of mercury, and when the mixture is evaporated, the acid escapes, and leaves the mercurial salt unchanged. When hydrofluoric acid is poured upon peroxide of mercury, it acquires an orange colour, and is dissolved upon the addition of water. The solution furnishes yellow prismatic crystals, which, by the action of hot water, are resolved into a soluble and insoluble compound.

Mercury and Nitric Acid.—Nitric acid is rapidly decomposed by mercury; nitrous acid, and nitric oxide gases are evolved, and either a protonitrate or a pernitrate of mercury are obtained, according to the mode in which the solution is performed.

Protonitrate of Mercury is best obtained by dissolving the metal in a cold and dilute acid, consisting of one part of acid and three of water; the metal should be added in small successive portions until the acid ceases to act upon it, and care should be taken to keep the whole cold. This solution deposits transparent crystals, which appear to be modified octoëdra, and which consist of the protoxide of mercury combined with nitric acid. They are soluble without decomposition in cold water, and the solution affords black precipitates of protoxide, upon the addition of excess of the alkalis. Small quantities of the caustic alkalis dropped into this solution, occasion yellowish and gray precipitates, which appear to be mixtures

of the oxide and subnitrate. The crystallized protonitrate consists, according to Mitscherlich, of

1 proportional of protoxide of mercury	.	.	= 208
1 „ nitric acid	.	.	= 54
2 proportionals of water (9×2)	.	.	= 18
			<hr/> 280

Pernitrate of Mercury.—When mercury is dissolved in hot and concentrated nitric acid, nitric oxide is evolved, the metal becomes peroxidized, and furnishes prismatic crystals of the pernitrate. They are soluble, without decomposition, in cold water, and their solution furnishes a yellow precipitate of hydrated peroxide of mercury, upon the addition of potassa or soda, and ammonia forms a white precipitate, which is a *triple nitrate of mercury and ammonia*.

The pernitrate of mercury should consist, according to theory, of

1 proportional of peroxide of mercury	.	.	= 216
2 proportionals of nitric acid (54×2)	.	.	= 108
			<hr/> 324

According to Thomson, the above crystals consist of one proportional of the peroxide, and one of nitric acid; and Mitscherlich states that the true neutral salt cannot exist in a solid form.

When the precautions in forming the nitrates above described are not attended to, the solution usually contains a mixture of the two nitrates, and furnishes a precipitate with the alkalis, composed of both oxides. The pernitrate is most certainly formed by dissolving the red oxide in nitric acid.

When hot water is poured upon pernitrate of mercury, a yellow insoluble powder separates from it, which is a *subpernitrate*, the *nitrous turpeth* of old writers; and a *superpernitrate* remains in solution. It seems probable that the protonitrate is also capable of affording a sub and a super nitrate; but all these compounds have hitherto been but imperfectly investigated, and new researches are wanting to establish their nature and composition. Grouvelle (*Ann. de Chim. et Phys.* xix.) found the yellow subpernitrate to consist of

2 proportionals of peroxide of mercury (216×2)	.	.	= 432
1 proportional of nitric acid	.	.	= 54
			<hr/> 486

When these nitrates of mercury are exposed to heat gradually raised to dull redness, nitric acid is given off; and a brilliant red substance remains, consisting of peroxide of mercury with a small portion of adhering nitrate. This is used in pharmacy as an escharotic, and is called in the *London Pharmacopæia*, *hydrargyri nitrico-oxidum*. The following are the directions for its preparation:—

Take of purified mercury, *by weight*, 3 lbs.
 „ nitric acid, *by weight*, a pound and a half.
 „ Distilled water, two pints.

Mix them in a glass vessel, and boil until the mercury being dissolved, and the water evaporated, a white substance remains. Rub this to powder, and put it into a very shallow vessel; then expose it to a moderate fire, gradually increased until red vapour ceases to escape.

In the first part of this process a pernitrates of mercury is formed, which is then decomposed by heat. It is very difficult so to apply the heat, as to expel the whole of the acid, without at the same time evolving oxygen from the remaining oxide and evaporating part of the mercury. We find, therefore, a small portion of nitric acid generally remaining in the compound. The nitrate requires to be constantly stirred during the process, which is generally performed in a cast-iron pot; the operator will find it advantageous to prepare the solution and partly to evaporate it in a retort with an annexed receiver containing a little water, by which, if any quantity of materials is employed, he will save a part of the acid.

The resulting nitrico-oxide of mercury is of a brilliant red colour, with a shade of orange; when not in very fine powder it has a glistening scaly appearance; at a red heat it is decomposed and entirely dissipated, provided it be not adulterated, as it sometimes is, with red lead: it has an acrid taste, is very sparingly soluble in water, and readily soluble without effervescence in nitric acid. The proportion of subpernitrate of mercury remaining in this preparation is variable; but some is always to be detected, for, when decomposed by heat, the evolved oxygen is found to be mixed with a portion of nitrogen: it therefore should never be used as a substitute for pure peroxide of mercury. When washed with and triturated

in a dilute solution of potassa, edulcorated with distilled water, and carefully dried, it may be regarded as nearly pure peroxide of mercury. In this state it is called *arcanum corallinum* in some of the older Pharmacopœiæ*.

Mercury and Sulphur.—When one part of mercury is triturated for some time with three of sulphur, a black tasteless compound is obtained, which was called in old pharmacy *Ethiops Mineral*; it is the *hydrargyri sulphuretum nigrum* of the present Pharmacopœia, and is often regarded as a definite sulphuret, but when boiled in solution of potassa, sulphur is taken up, and bisulphuret of mercury remains; so that it is probably a mixture of sulphur and of the bisulphuret. According to Taddei, an *Ethiops mineral* may be quickly formed by the following process. (*Gior. di Fisica*, iv. 12.) Put one part of sulphuret of potassa with three of mercury into a mortar, and triturate with a little water, until the whole forms a homogeneous black paste; then add flowers of sulphur equal in weight to the mercury, and mix the whole; wash with repeated affusions of water, till the alkaline sulphuret is removed, and carefully dry the remaining *ethiops*.

When sulphuretted hydrogen is passed through a dilute solution of protonitrate of mercury, a black powder is thrown down, which is a true sulphuret, and which, according to Guibourt (*Ann. de Chim. et Phys.*, tom. i.), consists of 100 mercury + 8.2 sulphur, numbers which correspond to

1 proportional of mercury	= 200
1 „ sulphur	= 16
									<hr/>
Equivalent of sulphuret of mercury	= 216

When this sulphuret is boiled with nitric acid, it is converted into a sulphate of mercury: heated to redness, metallic mercury escapes, and bisulphuret sublimes.

Bisulphuret of Mercury, when recently sublimed, is of a steel gray colour, but when reduced to a fine powder, it assumes a brilliant red colour, and is called *vermilion*, or *cinnabar*. It consists of

1 proportional of mercury	= 200
2 proportionals of sulphur (16 × 2)	= 32
									<hr/>
Equivalent of bisulphuret of mercury	= 232

* Disp. Boruss. Brand. 1731.

In the manufacture of cinnabar, eight parts of mercury are mixed in an iron pot with one of sulphur, and made to combine by a moderate heat, and constant stirring: this compound is then transferred to a glass subliming vessel (on a small scale, a Florence flask answers perfectly), and heated to redness in a sand bath; a quantity of mercury and of sulphur evaporate, and a sublimate forms, which is removed, and rubbed or levigated into a very fine powder. If mercury and sulphur be heated together in large quantities, the action is so intense at the moment of their combination as to occasion a slight explosion and flame; sulphuretted hydrogen is also evolved.

Cinnabar is not altered by exposure to air or moisture; when heated to dull redness in an open vessel, the sulphur forms sulphurous acid, and the mercury escapes in vapour. It is decomposed by distillation with fixed alkalis, lime, and baryta, and by several of the metals. When adulterated with red lead it is not entirely volatile. It is insoluble in nitric and muriatic acids, but nitromuriatic acid acts upon, and decomposes it even in the cold. Boiled in sulphuric acid, sulphurous acid is evolved, and a sulphate of mercury formed.

Cinnabar may be made in the humid way by long trituration of mercury and sulphur in solution of potassa.—Nicholson's *Journal*, 4to. ii. When a solution of corrosive sublimate is added to excess of hydrosulphuret of ammonia, a black precipitate falls, which acquires the colour of cinnabar when sublimed.

Native Cinnabar is the principal ore of mercury: it occurs massive and crystallized in six-sided prisms, rhombs, and octoëdra. It is of various colours, sometimes appearing steel gray, at others bright red. It occurs in Hungary, France, and Spain, in Europe; in Siberia, and Japan, in Asia; and in considerable quantities in South America. The mines of Almaden, and of New Spain, are the most productive, and furnish fine cabinet specimens. Native mercury, and native amalgam of silver sometimes accompany it.

Hypsulphites of Mercury.—When a solution of a hypsulphite is poured into a very dilute solution of protonitrate of mercury it occasions a black precipitate, which, however, is probably not a true hypsulphite. The nature of these compounds has not been satisfactorily ascertained.

Sulphites of Mercury have not been examined.

Mercury and Sulphuric Acid.—When one part of mercury is digested in a moderate heat with one and a half of sulphuric acid, sulphurous acid gas is evolved, and a white deliquescent mass is obtained, which, washed with cold water, affords a very difficultly soluble white salt, which is a *protosulphate of mercury*. It requires 500 parts of cold and 300 of boiling water for its solution, and crystallizes in prisms. According to Fourcroy, it is soluble in dilute sulphuric acid, and thus forms a crystallizable supersulphate. Its solution in boiling water is decomposed by the alkalis, which first throw down a subsalt, and when added in excess separate the black protoxide. This salt consists of

1	proportional of protoxide of mercury	= 208
1	„ sulphuric acid	= 40
	Equivalent of protosulphate of mercury	= 248

If five parts of sulphuric acid be boiled to dryness with four of mercury, a white crystalline mass of *persulphate of mercury* is obtained, composed of

1	proportional of peroxide of mercury	= 216
2	proportionals of sulphuric acid (40×2)	= 80
	Equivalent of persulphate of mercury	= 296

This salt cannot exist in solution in the neutral state, for water resolves it into a soluble supersalt and an insoluble subsalt. The soluble portion may be obtained by evaporation in the form of deliquescent acicular crystals. The subsalt, when triturated with boiling water, acquires a yellow colour, and was formerly called *turpeth mineral*, from a similarity in its medical effects to the roots of the *convolvulus turpethum*: it is dangerously cathartic and emetic. It is not absolutely insoluble in water, but requires 2000 parts of cold and 300 boiling water for the purpose.

Ammonio-persulphate of Mercury is obtained in the form of a white and very difficultly soluble powder, by adding excess of ammonia to the persulphate.

The fixed alkalis throw down from the persulphate a yellow precipitate of hydrated peroxide of mercury.

Sulphuretted hydrogen produces a black precipitate in all the solutions of mercury when added in excess, and which ap-

pears to be a sulphuret of mercury, containing variable proportions of sulphur and metal, according to the degree of oxidizement in which the mercury existed in the solution. When calomel is decomposed by excess of sulphuretted hydrogen, it affords a black powder, convertible by heat into metallic mercury and cinnabar. Corrosive sublimate under the same circumstances affords a precipitate not differing from the former in appearance, but which, when heated, affords cinnabar only. (Guibourt, *Ann. de Chim. et Phys.* i. 424.) According to this authority, there is only one sulphuret of mercury, composed of one proportional of metal, and two of sulphur; but, from what has been stated under the head of sulphurets of mercury, it can scarcely be doubted that the precipitate formed in the true protosalts of mercury by excess of sulphuretted hydrogen, is a compound of one proportional of metal and one of sulphur.

Phosphuret of Mercury may be formed by heating phosphorus with oxide of mercury. It is a sectile solid of a bluish black colour.

Neither the *Hypophosphite* nor *Phosphite of Mercury* have been examined.

Phosphates of Mercury.—When phosphate of soda is dropped into protonitrate of mercury, a white crystalline precipitate falls, which is *protophosphate of mercury*. It is insoluble in water and in excess of phosphoric acid, and when intensely heated is decomposed, and leaves phosphoric acid. *Perphosphate of mercury* is thrown down from the pernitrates by the addition of phosphate of soda: it resembles the protophosphate in appearance, but it dissolves in excess of phosphoric acid.

Seleniuret of Mercury is a tin coloured substance, which sublimes in shining scales at a temperature below its point of fusion.

Biseleniuret of Mercury is obtained as a gray crystalline mass, by fusing the seleniuret with selenium.

Carbonates of Mercury.—When solution of carbonate of potassa is dropped into protonitrate of mercury, a white *protocarbonate of mercury* is thrown down, which dissolves in excess of carbonic acid and of the carbonated alkali. The *percarbonate of mercury* is of a reddish colour.

Mercury and Cyanogen.—By boiling one part of finely powdered red oxide of mercury with two of Prussian blue, in eight parts of water, a solution is obtained, which, if filtered while hot, deposits, on cooling, yellowish-white crystals in the form of quadrangular prisms, of a metallic taste and very poisonous, consisting, according to Gay-Lussac, of 80 mercury + 20 cyanogen. They are, therefore, a *bicyanuret of mercury*, and probably contain

1 proportional of mercury	=	200
2 proportionals of cyanogen (26×2)	=	52
Equivalent of cyanuret of mercury	=	252

Cyanuret of mercury is much more soluble in hot than in cold water. It is very sparingly soluble in alcohol. When oxide of mercury is brought into the contact of the vapour of hydrocyanic acid they act intensely upon each other, and water and cyanuret of mercury are immediately formed. The attraction of mercury for cyanogen is so strong, that peroxide of mercury decomposes nearly all the metallic cyanurets, not excepting that of potassium. The salts of palladium, however, decompose the cyanuret of mercury.

Cyanuret of mercury is decomposed by heat, as in the process for obtaining cyanogen; and if distilled with muriatic acid, hydrocyanic acid and chloride of mercury are formed. It also is decomposed by hydriodic acid and by sulphuretted hydrogen, an iodide and a sulphuret of mercury, and hydrocyanic acid, being formed. Nitric acid dissolves it without decomposition. It is decomposed when heated with sulphuric acid. The alkalis do not act upon this cyanuret.

Cyanuret of mercury is also formed by boiling peroxide of mercury in solution of ferrocyanate of potassa; a portion of mercury and of peroxide of iron are at the same time deposited, whence it appears that the oxygen of the mercurial oxide is partly transferred to the iron, and partly to the hydrogen of the ferrocyanic acid.

Cyanuret of mercury boiled in water with peroxide of mercury produces a compound which forms small granular crystals consisting of cyanuret and oxide of mercury; hence, in making the cyanuret by the above process, excess of mercurial oxide should be avoided.

When cyanuret of mercury and iodide of potassium are mixed together in solution, pearly crystals are thrown down, which, when redissolved and crystallized, form large thin and brilliant plates, requiring 16 parts of water at 60° for their solution. When strongly heated they are decomposed, leaving a residue of iodide of potassium blackened with charcoal. (*Ann. de Chim. et Phys.* xix. 220.)

Fulminating Mercury. Liebig's *Cyanate of Mercury*.—This compound was discovered by Mr. Howard. (*Phil. Trans.* 1800, p. 214.) It is prepared by dissolving 100 grains of mercury in a measured ounce and a half of nitric acid, aided by heat. This solution is to be poured, when cool, into two measured ounces of alcohol in a glass basin, and gently warmed: it soon begins to effervesce and evolve ethereal vapour, and if the action is too violent, it must be quelled by cooling the vessel, or by the addition of a little cold alcohol. During this action a yellow-gray precipitate falls, which is to be immediately separated by decantation and filtration, washed with small quantities of distilled water, and carefully dried at a heat not exceeding 212° . The above quantity of mercury yields about 120 grains of the powder when the operation has been most successful.

This compound, when heated to about 300° , explodes with a bright flame: it also detonates by friction, by the electric spark, and by contact of concentrated sulphuric and nitric acids: the gases evolved at its explosion are carbonic acid, nitrogen, and a little ammonia. Liebig and Gay-Lussac have furnished some curious facts towards the history of this compound (*Ann. de Chim. et Phys.* xxiv. and xxv.), showing that, like the corresponding fulminating silver, it consists of protoxide of mercury in combination with a peculiar acid. (See SILVER.)

Borates of Mercury.—When solution of protonitrate of mercury and of borate of soda are mixed and evaporated, small shining crystals of *protoborate of mercury* are obtained. Boracic acid occasions no precipitates in solution of pernitrates of mercury.

The *Perborate of Mercury* has not been examined.

Arseniales of Mercury.—Arsenic acid occasions a pale yellow precipitate in solution of protonitrate of mercury, and a yel-

lowish white precipitate in solution of the pernitrate. Arsenious acid produces white precipitates in both solutions. These precipitates are soluble in muriatic acid.

Molybdic Acid occasions a yellow precipitate in solution of protonitrate of mercury, easily soluble in nitric acid.

Chromate of Mercury.—Chromate of potassa throws down an orange-coloured precipitate from the solutions of nitrate and pernitrate of mercury.

Tungstate of Mercury.—Not examined.

The soluble salts of mercury furnish whitish precipitates with ferrocyanate of potassa, and black with sulphuretted hydrogen. A plate of copper, immersed into their solutions, occasions the separation of metallic mercury.

The insoluble mercurial salts are mostly entirely volatilized at a red heat; if distilled with charcoal, they afford metallic mercury.

Mercury combines with most of the other metals, and forms a class of compounds which have been called *amalgams*. Many of these are definite and crystallizable compounds, and may be separated by gentle pressure from the mercury, in which the definite compound is suspended or dissolved. These are generally brittle or soft. One part of potassium with 70 of mercury produce a hard brittle compound. If mercury be added to the liquid alloy of potassium and sodium, an instant solidification ensues, and heat enough to inflame the latter metals is evolved. The use of an amalgam of zinc and mercury has already been adverted to for the excitation of electrical machines. The amalgams of gold and silver are employed in gilding and plating. An amalgam of two parts of mercury, one of bismuth, and one of lead, is fluid, and when kept for some time deposits cubic crystals of bismuth. Amalgam of copper may be made as follows: To a hot solution of sulphate of copper, add a little muriatic acid and a few sticks of zinc, and boil the mixture for about a minute: by this means the copper will be precipitated in a metallic state, and in a finely divided spongy form: take out the zinc, pour off the liquor, wash the copper with hot water, and pour upon it a little dilute nitrate of mercury, which will instantly cover every particle of copper with a coating of mercury: then add mercury to the amount of two or three times the weight of the copper, and a slight

trituration will combine them so far that the completion of the process may be effected by heating the mixture for a few minutes in a crucible.—Aikin's *Dictionary*—Art. MERCURY.

Antimony and tellurium combine difficultly with mercury into granular compounds. Amalgam of arsenic was obtained by Bergman by digesting one part of powdered arsenic with five of quicksilver, and frequently agitating the mixture.

Amalgam of Ammonia.—When mercury is negatively electrized in a solution of ammonia, or when an amalgam of potassium and mercury is placed upon moistened muriate of ammonia, the metal increases in volume, and becomes of the consistency of butter, an appearance which has sometimes been called the *metallization of ammonia*. The compound appears only to contain ammonia and mercury, though its real nature has not been satisfactorily ascertained. It has suggested some hypotheses concerning the nature of ammonia and the metals, which are scarcely worth recording. Upon this subject, however, the reader may consult Gay-Lussac and Thenard (*Recherches Physico-Chimiques*, vol. i.), who, finding the amalgam resolvable into mercury, ammonia, and hydrogen, regard it merely as a compound of those substances; and Berzelius (*Lehrbuch*, i.), who considers the appearances as resulting from the combination of a metal, which he terms *ammonium*, with the mercury.

Section XXIX. SILVER.

SILVER is found native, and in a variety of combinations.

Native Silver has the general characters of the pure metal. It occurs in masses; arborescent; capillary; and, sometimes, crystallized in cubes and octoëdra. It is seldom pure, but contains small portions of other metals, which affect its colour and ductility. It is chiefly found in primitive countries. In Peru and Mexico are the richest known mines of native silver. The mines of Saxony, Bohemia, and Swabia, and those of

Kongsberg in Norway, are the richest in Europe. It has been found in Cornwall and Devonshire.

Pure silver may be procured by dissolving the standard silver of commerce in pure nitric acid, diluted with an equal measure of water. Immerse a plate of clean copper into the solution, which soon occasions a precipitate of metallic silver; collect it upon a filter; wash it with solution of ammonia, and then with water, and fuse it into a button.

It may also be procured by adding to the above solution of standard silver a solution of common salt; collect, wash, and dry the precipitate, and gradually add it to twice its weight of fused carbonate of potassa in a red-hot crucible. Metallic silver is separated, and may be fused into a button.

Silver has a pure white colour, and considerable brilliancy. Its specific gravity is 10.5. It is so malleable and ductile, that it may be extended into leaves not exceeding a ten-thousandth of an inch in thickness, and drawn into wire finer than a human hair.

Silver melts at a bright red heat, and when in fusion appears extremely brilliant. It resists the action of air at high temperatures for a long time, and does not oxidize; the *tarnish* of silver is occasioned by sulphureous vapours; it takes place very slowly upon the pure metal, but more rapidly upon the alloy with copper used for plate, and was found by Proust to consist of sulphuret of silver. Pure water has no effect upon the metal; but if the water contain vegetable or animal matter, it often slightly blackens its surface in consequence of the presence of sulphur. If an electric explosion be passed through fine silver wire, it burns into black powder, which is an oxide of silver. In the Voltaic circle it burns with a fine green light, and throws off abundant fumes of oxide. Exposed to an intense white heat, it boils and evaporates. If suddenly cooled, it crystallizes during congelation, often shooting out like a cauliflower, and throwing small particles of the metal out of the crucible. This arises, according to Lucas, from the sudden escape of a minute quantity of oxygen, which the metal absorbs, and is prevented by the presence of a minute quantity of copper.

Silver is not unfrequently obtained in considerable quantities from argentiferous sulphuret of lead, which is reduced in

the usual way, and then *cupelled*: the oxide of lead thus procured is afterwards reduced by charcoal. Some of the silver ores, especially the sulphurets, are reduced by amalgamation. These ores, when washed and ground, are mixed with a portion of common salt and roasted; it is then powdered and mixed by agitation with mercury, and the amalgam thus formed is distilled. The old process of *eliquation* is now scarcely used: it consisted in fusing alloys of copper and silver with lead; this triple alloy was cast into round masses, which were set in a proper furnace upon an inclined plane of iron with a small channel grooved out, and heated red-hot, during which the lead melted out, and, in consequence of its attraction for silver, carried that metal with it, the copper being left behind in a reddish black spongy mass.—Aikin's *Dictionary*—
Art. SILVER.

Oxide of Silver may be obtained by adding lime-water or dilute solution of potassa to the solution of nitrate of silver, and washing the precipitate. It is of a dark olive colour, tasteless, insoluble in water, and when gently heated, is reduced to the metallic state. Long exposure to light also reduces it, converting it into a black powder, which is either silver or its suboxide. It confers a yellow colour upon glass, and is employed in enamel and porcelain painting.

The composition of oxide of silver has been very variously given, probably from the difficulty of obtaining it of similar purity. If its composition be inferred from the chloride, or from the sulphuret, we obtain the number 110 as the representative of silver, and the protoxide will consist of

1	proportional of silver	=	110
1	„ oxygen	=	8
							<hr/>
	Equivalent of protoxide of silver	=	118

By a direct experiment upon the oxide of silver, precipitated by potassa from the nitrate, nearly the same equivalent number was obtained.

This is the only salifiable oxide of silver; but Mr. Faraday has rendered it probable that there is another combination of silver and oxygen, containing a smaller proportion of oxygen than the above, which may be called a *suboxide*. He obtained it in the form of a black film, by exposing an ammoniacal solu-

tion of oxide of silver to the air; and Ritter, by electrizing a weak solution of silver, observed the deposition of acicular crystals at the positive pole, which, according to Grotthuss, dissolve in nitric acid, without decomposition, and are a *peroxide of silver*. Ammonia energetically decomposes this compound, and sulphuric and phosphoric acids convert it into the protoxide.

Oxide of silver readily dissolves in ammonia, and by particular management, a *fulminating silver*, composed of the oxide combined with ammonia, may be obtained. It was discovered by Berthollet. (*Annales de Chimie*, tom. i.) The best process for obtaining it is to pour a small quantity of liquid ammonia upon the oxide; a portion is dissolved, and a black powder remains, which is the detonating compound. It explodes when gently heated; nitrogen and water are instantaneously evolved, and the silver is reduced. The oxide of silver should be perfectly pure and thoroughly edulcorated, and the ammonia quite free from carbonic acid. It should only be prepared in small quantities, and handled with the greatest caution, many accidents having arisen from its careless management. It sometimes explodes while still wet.

Silver and Chlorine—Chloride of Silver.—This compound is easily procured by adding a solution of chlorine, of muriatic acid, or of common salt, to a solution of nitrate of silver, or, indeed, to any of the soluble salts of silver, with the exception of the hyposulphite. It falls in the form of a heavy insoluble tasteless powder, of a white colour, but which, by exposure to light, becomes brown, and ultimately black. The minutest portion of muriatic acid, or of a chloride in solution, may be detected by adding to the liquid a drop or two of nitrate of silver; it becomes opalescent, and brown by exposure to light. It is sparingly dissolved by concentrated muriatic acid, and thrown down upon dilution. When dry chloride of silver is heated to dull redness in a silver crucible it does not lose weight, but fuses, and, on cooling, concretes into a grey semi-transparent substance, which has been called *horn silver*, or *luna cornea*. If slowly cooled, Proust has remarked that it has a tendency to octoëdral crystallization. Heated to a bright red or white heat in an open vessel, it volatilizes in dense white fumes. Scheele was the first who examined the cause of the

blackening effect of light upon this chloride, and the curious results of his researches have already been referred to. (Vol. i. p. 125.) He found that the metal was partially reduced, and muriatic acid formed; hence moisture is necessarily present. Seebeck found that white chloride of silver might be exposed, without change of colour, when covered in a stopped phial, with sulphuric acid; but if the phial was open, the blackening ensued; as it did also when water was added. Common hydrogen gas, and substances affording hydrogen, decompose moist chloride of silver: they reduce it to the metallic state, and the chlorine is carried off in the form of muriatic acid; but in the dark, perfectly pure hydrogen does not discolour the chloride.

If fused with twice its weight of potassa or soda, chloride of silver is decomposed, and a globule of metallic silver is obtained. It is also rapidly decomposed by tin and zinc. Triturated with zinc filings and moistened, the heat produced is so considerable as to fuse the resulting alloy of zinc and silver. (Faraday, *Quarterly Journal of Science and Arts*, viii. 374.)

Chloride of silver is very soluble in ammonia, a circumstance by which it is usefully distinguished from some other chlorides, which, like it, are white, and formed by precipitation. We should be cautious in applying heat to the ammoniacal solution, as it sometimes forms a precipitate of fulminating silver. The ammoniacal solution furnishes crystals, which, when exposed to air, or put into water, lose their transparency, ammonia is evolved, and they crumble into chloride of silver. The fused chloride, exposed to ammoniacal gas, absorbs a considerable portion, which is given off by heat. If the dry chloride, thus saturated with ammonia, be thrown into chlorine, the ammonia spontaneously inflames. (Faraday, *Journal of Science and Arts*, vol. v. p. 75.) Chloride of silver is soluble in and decomposed by all the liquid hyposulphites.

As chloride of silver is insoluble in water, and very readily formed, it is often employed in analysis, as a means of ascertaining the proportion of chlorine present in various compounds. In these cases some excess of the precipitant should be used, and the precipitate allowed to subside previous to separating it upon the filter: if the supernatant liquor become perfectly clear, the whole of the silver has fallen; if it remain

opalescent, a portion is probably still retained. When the precipitate remains long suspended, its deposition may be accelerated by warmth, or by adding a little nitric acid. The chloride in these cases should be perfectly dried in a silver crucible, up to incipient fusion.

The following are three of the best analyses of chloride of silver, and their close correspondence is no small test of their accuracy.

	Marcet.	Gay-Lussac.	John Davy.
Silver	75.47	75.25	75.5
Chlorine	24.53	24.75	24.5
	<hr/> 100.	<hr/> 100.	<hr/> 100.

The mean composition deduced from these experiments may be called

Silver	75.4
Chlorine	24.6
	<hr/> 100.

And we may accordingly, without material error, consider the chloride of silver as composed of

1 proportional of silver	= 110
1 " chlorine	= 36
	<hr/>
Equivalent of chloride of silver	= 146

Native Chloride of Silver has been found in most of the silver mines; it occurs massive and crystallized in small cubes and octoëdra.

Chlorate of Silver is formed by digesting oxide of silver in chloric acid: it forms small rhombic crystals, which, by the action of chlorine, are converted into chloride of silver. They are soluble in four parts of water at 60°.

Muriatic Acid has no action upon a piece of clean silver, unless boiled with it for a long time, when a slight crust of chloride forms upon it. A beautiful experiment, illustrating the influence of electricity on chemical action, consists in attaching a slip of silver to each pole of the Voltaic pile and immersing them in dilute muriatic acid; that which is negative remains clean and bright, but that which is positive attracts the chlorine, and is immediately covered with a white crust. In the same way the positive silver becomes speedily oxidized

when immersed in water ; while the negative silver evolves hydrogen, and remains clean.

Iodide of Silver is precipitated upon adding hydriodic acid, or a soluble iodide, to a solution of nitrate of silver. It is of a greenish yellow colour, insoluble in water, and decomposed when heated with potassa. It is particularly characterized by being nearly insoluble in ammonia. When fused it acquires a red colour. It consists of

1	proportional of silver	=	110
1	„ iodine	=	125
						<hr/>	235

Iodate of Silver is precipitated in the form of a white powder by adding iodic acid or iodate of potassa to a solution of nitrate of silver. It is very soluble in ammonia. It is decomposed by sulphurous acid, which throws down iodide of silver, and becomes sulphuric acid.

Bromide of Silver is an insoluble white substance thrown down upon the addition of bromine or hydrobromic acid, or the soluble bromides to nitrate of silver. It dissolves in ammonia.

Bromate of Silver.

Fluoride of Silver is a soluble compound, which does not crystallize. When heated it fuses ; and at a higher temperature, and exposed to air, it is slowly reduced.

Nitrate of Silver.—Nitric acid, diluted with three parts of water, readily dissolves silver, with the disengagement of nitric oxide gas. If the acid contain the least portion of muriatic, the solution will be turbid, and deposit a white powder ; and if the silver contain copper, it will have a permanent greenish hue ; or if gold, that metal will remain undissolved in the form of a black powder.

The solution of nitrate of silver should be perfectly clear and colourless ; it is caustic, and tinges animal substances of a deep yellow, which, by exposure to light, becomes a deep purple, or black stain, and is indelible, or peels off with the cuticle : it consists of reduced silver. It may be obtained in white crystals, in the form of four and six-sided tables, of a bitter and metallic taste, and soluble in about their own weight of water at 60°. Alcohol also dissolves about one-fourth its

weight of this salt, at its boiling point, but deposits nearly the whole as it cools. Crystallized nitrate of silver is anhydrous, and consists of

1	proportional of oxide of silver	.	.	.	= 118
1	„ nitric acid	.	.	.	= 54
					<hr/>
	Equivalent of nitrate of silver	.	.	.	= 172

According to Proust (Nicholson's *Journal*, xv. 376), a solution of this nitrate, when boiled with finely divided silver, dissolves a portion, and yields a solution containing a suboxide of silver.

Nitrate of silver blackens when exposed to light, and when thus acted upon, is no longer perfectly soluble in water, owing to the separation of a portion of metallic silver.

When heated in a silver crucible it fuses into a grey mass, and if cast into small cylinders, forms the *lapis infernalis*, or *lunar caustic* of pharmacy; the *argenti nitras* of the *Pharmacopæia*. In forming this preparation, care should be taken not to overheat the salt, so as to blacken it, and the moulds should be warmed. Exposed to a red heat, the acid is partly evolved and partly decomposed, and metallic silver obtained. Sulphur, phosphorus, charcoal, hydrogen, and several of the metals, decompose this nitrate. A few grains mixed with a little sulphur, and struck upon an anvil with a heavy hammer, produce a detonation; phosphorus occasions a violent explosion when about half a grain of it is placed upon a crystal of the nitrate, upon an anvil, and struck sharply with a hammer; and if heated with charcoal it deflagrates, and the metal is reduced. If a piece of silk dipped into a solution of nitrate of silver be exposed, while moist, to a current of hydrogen gas, it is first blackened, and afterwards becomes iridescent from the reduction of portions of the metal. (Mrs. Fulhame's *Essay on Combustion*.) Ivory, marble, and several other bodies, may be stained black, or even silvered, by soaking them in a solution of nitrate of silver, and fully exposing them to the action of the sun's rays. When the vapour of pure distilled water is made to pass through nitrate of silver, the solution assumes all the shades between yellow and dark brown, according to its concentration and the time the steam has passed through it. When it has acquired the temperature of 212° , its colour increases rapidly. Nitric acid immediately destroys this colour,

the cause of which is referred by Professor Pfaff to the de-oxidizing agency of the steam. (*Quarterly Journal*, xvi. 162.) A stick of phosphorus, introduced into a solution of nitrate of silver, soon becomes beautifully incrustated with the metal, which separates upon it in arborescent crystals. A plate of copper occasions a brilliant precipitation of silver, and the copper is oxidized and dissolved by the acid. Mercury introduced into the solution of nitrate of silver, causes a beautiful crystalline deposit of silver, called the *arbor Dianæ*: it was first remarked by Lemery. To obtain this crystallization in its most perfect state, the solution should contain a little mercury, and the mercury put into it should be alloyed with a little silver. Baumé directs an amalgam of one part of silver with seven of mercury, of which a small piece is to be introduced into a solution composed of six drachms of saturated nitrate of silver and four drachms of a similar solution of mercury diluted with five ounces of distilled water: a small flask or matrass should be used for the experiment, kept perfectly at rest: in a few minutes small filaments of silver darken the surface of the amalgam, and in about eight and forty hours the whole has separated in a shrub-like form. The principal use of the addition of mercury to the solution, and of silver to the precipitating mercury, is to give a degree of tenacity to the arborescent deposit of crystals, which prevents their falling to the bottom of the flask.

The alkaline metallic oxides decompose this salt of silver; it is also decomposed by muriatic, sulphuric, phosphoric, and boracic acid. The protosulphate of iron throws down metallic silver when added to a solution of the nitrate: protomuriate of tin forms a grey precipitate consisting of peroxide of tin and oxide of silver. Ammonia, added to solution of nitrate of silver, occasions a precipitate, soluble in excess of the alkali. (See Berthollet's *FULMINATING SILVER*, p. 179).

Nitrate of silver is of much use, as a test for chlorine, muriatic acid, and their compounds. It is employed for writing upon linen under the name of *indelible* or *marking ink*, which may be prepared by dissolving two drachms of pure nitrate of silver and one drachm of gum arabic in seven drachms of distilled water, coloured by a little China ink. The preparatory liquid for moistening the cloth is made by dissolving two

ounces of crystallized carbonate of soda and two drachms of gum arabic in four ounces of water. It is an ingredient in many of the liquids which are sold for the purpose of changing the colour of hair. It is used in medicine and in surgery as an excellent caustic. When taken internally, a very disagreeable effect frequently follows its use, which is the discolouration of the *rete mucosum*; so that the whole surface of the body, and especially the parts most exposed to light, acquire a leaden-grey or livid colour, which is permanent, and can neither be removed nor prevented.

Nitrite of Silver is obtained, according to Berzelius, by long digestion of powdered silver in nitric acid already saturated with the metal. It is more soluble than the nitrate, and difficultly crystallizable. It is the same salt as that which Proust regarded as a nitrate of a suboxide (see p. 183): it appears not improbable that it may contain the suboxide noticed by Mr. Faraday.

Sulphuret of Silver.—Silver readily combines with sulphur, and produces a gray crystallizable compound, considerably more fusible and much softer than silver. It is this which forms the *tarnish* upon silver plate. It consists of

1 proportional of silver	= 110
1 „ sulphur	= 16
					<hr/>
Equivalent of sulphuret of silver	= 126

Sulphuretted hydrogen and hydrosulphuret of ammonia occasion a copious black precipitate of sulphuret of silver when added to solutions of the metal: a portion of the silver is frequently at the same time reduced to the metallic state.

Native Sulphuret of Silver, or *vitreous silver ore*, is found in various forms, and when crystallized, is in cubes, octoëdra, and dodecaëdra. It is soft and sectile. The finest specimens are from Siberia.

A triple combination of silver and antimony with sulphur constitutes the *red or ruby silver ore*; it is found massive and crystallized in hexaëdral prisms. It consists of about 70 parts of sulphuret of silver, and 30 sulphuret of antimony; or, according to Berzelius, of

Silver	55.98
Antimony	23.46
Sulphur	17.56
						<hr/>
						100

It occurs in all the silver mines, and is sometimes accompanied by the *brittle sulphuret of silver*, or *silver glance*.

Hyposulphite of Silver has been examined by Mr. Herschel in his able paper on the hyposulphurous acid. (*Edin. Phil. Journal*, i. 26.) It is formed by dropping a weak solution of nitrate of silver into a very dilute solution of hyposulphite of soda: a white cloud is at first produced, which redissolves on agitation; on adding more of the precipitant, the cloud re-appears and aggregates into a grey precipitate, which appears to consist of hyposulphite of silver; the supernatant liquor tastes intensely sweet, which is remarkable, considering the disgusting bitterness both of the nitrate and of the hyposulphite, and shows, says Mr. Herschel, "how little we know of the way in which bodies affect the organs of taste. Sweetness and bitterness, like acidity, seem to depend upon no particular principle, but to be regulated by the state of combination in which the same principles exist at different times." Hyposulphite of silver is also produced when chloride of silver is dissolved in any of the hyposulphites; the solution is intensely sweet without any metallic flavour. These facts show the strong affinity that exists between oxide of silver and hyposulphurous acid.

Hyposulphite of Potassa and Silver is formed when liquid potassa is dropped into the solution of chloride of silver in hyposulphite of soda; it separates in the form of a copious precipitate, which, when washed and dried, is found to consist of small grey pearly scales; they are difficultly soluble in water; of a very sweet taste; and, heated before the blowpipe, afford a bead of silver. Several other analogous triple salts have been described by Mr. Herschel.

Sulphite of Silver is obtained in crystalline grains by digesting oxide of silver in sulphurous acid, or by adding an alkaline sulphite to a solution of silver. It produces triple salts with the sulphites of the alkalis. According to Fourcroy, it is not blackened by exposure to light, nor altered by air.

Hyposulphate of Silver is formed by digesting carbonate of

silver in hyposulphuric acid : it crystallizes in permanent prismatic crystals, soluble in two parts of cold water, and contains two proportionals of water of crystallization. Excess of ammonia added to a solution of this salt occasions a gradual precipitation of crystalline grains, consisting of an *ammonio-hyposulphate of silver*.

Sulphate of Silver is deposited when sulphate of soda is mixed with nitrate of silver. It is also formed by boiling silver with its weight of sulphuric acid. It forms a white saline mass, easily fusible. It requires about 90 parts of water at 60° for its solution ; in boiling water it is more soluble, and is deposited, as the solution cools, in small prismatic crystals : it is decomposed at a red heat, and leaves metallic silver. It is anhydrous, and consists of

1	proportional of oxide of silver	=	118
1	„ sulphuric acid	=	40
								<hr/>
	Equivalent of sulphate of silver	=	158

Upon the large scale, small portions of gold may be most economically separated from large quantities of silver, by heating the finely granulated alloy in sulphuric acid : the gold remains in the form of a black powder, and the sulphate of silver may be decomposed by the action of metallic copper ; the silver is precipitated in a pulverulent state, and, with a little borax or other vitrifiable flux, is fused, and cast into ingots ; the sulphate of copper is easily obtained in the crystallized state by evaporating the residuary liquid.

A compound acid, which may be called *nitro-sulphuric*, consisting of one part of nitre dissolved in about ten of sulphuric acid, dissolves silver at a temperature below 200°, and the solution admits of moderate dilution before sulphate of silver separates from it. This acid scarcely acts upon copper, lead, or iron, unless diluted with water ; it is, therefore, useful in separating the silver from old plated articles : the precious metal may afterwards be separated either in the form of chloride, by adding common salt ; or by diluting the acid and continuing the immersion of the pieces of copper which have lost their silvering, and which will now dissolve in the diluted acid, and occasion the precipitation of metallic silver.—Keir, *Phil. Trans.*, lxxx.

Phosphuret of Silver is a white brittle compound.

Neither *Hypophosphite* nor *Phosphite of silver* have been examined: it is, indeed, probable that the oxide of silver would be reduced by these acids.

Phosphate of Silver is formed by dropping a solution of phosphate of soda into nitrate of silver. It is of a yellow colour, and consists, according to Berzelius (*Ann. de Chim. et Phys.* tom. ii.), of

$$\begin{array}{r} 83 \text{ oxide of silver} \\ 17 \text{ phosphoric acid} \\ \hline 100 \end{array}$$

He regards it as a subphosphate, and says that it is converted into a difficultly crystallizable neutral salt, by digestion in phosphoric acid; but from the composition of the salt above stated, it closely approaches to

$$\begin{array}{rcl} 1 \text{ proportional of oxide of silver} & . & = 118 \\ 1 \text{ „ phosphoric acid} & . & = 28 \\ & & \hline & & 136 \end{array}$$

and the other is probably a *biphosphate*: it must be recollected, however, that our equivalent of phosphoric acid differs from that of Berzelius. (See vol. I. p. 278.)

Seleniuret of Silver, obtained by precipitation, is a black powder, which fuses into a globule having a metallic lustre. It consists of 73.16 silver, 26.84 selenium. When silver is fused with selenium, a grey *biseleniuret* is formed, from which the excess of selenium may be expelled by heat.

Selenite of Silver is thrown down, in the form of a white powder, very sparingly soluble in hot water. It is fusible, and at a high heat gives out selenious acid and oxygen, and leaves metallic silver. It is not discoloured by exposure to daylight.

Carbonate of Silver is precipitated in the form of a white insoluble powder, by adding carbonate of potassa to nitrate of silver. It blackens by exposure to light. It consists of

$$\begin{array}{rcl} 1 \text{ proportional of carbonic acid} & . & = 22 \\ 1 \text{ „ oxide of silver} & . & = 118 \\ & & \hline \text{Equivalent of carbonate of silver} & . & = 140 \end{array}$$

Carbonate of ammonia only throws down a portion of the

silver from the nitrate, and forms a triple *ammonio-carbonate of silver*.

Borate of Silver is thrown down from the nitrate of silver in the form of a white crystalline powder, by adding solution of boracic acid. It is very difficultly soluble in water.

Hydrocyanic Acid and hydrocyanate of potassa cause a white precipitate in solutions of silver, which appears to be a *cyanuret of silver*, and which, when heated, gives out cyanogen. It is insoluble in water, but readily soluble in ammonia. It is easily decomposed by muriatic acid; but sulphuric and nitric acids scarcely act upon it. Ferrocyanate of potassa throws down a white precipitate in solutions of silver.

Arsenite of Silver is precipitated in the form of a yellow powder, soon becoming grey and brown, by the addition of solution of arsenious acid to nitrate of silver. Nitrate of silver has already been adverted to as a test for white arsenic (p. 126).

Arsenate of Silver is thrown down from nitrate of silver by arsenic acid, of a reddish-brown colour. At a red heat, this compound evolves oxygen and arsenious acid, and arsenical silver remains.

Molybdate of Silver and *Tungstate of Silver* are precipitated in the form of white powder, insoluble in water.

Chromate of Silver is precipitated of a crimson colour by adding chromate of soda to nitrate of silver. It soon loses its brilliant tint and becomes brown. It dissolves in nitric acid.

Antimoniate, Tellurate, and Columbate of Silver, are insoluble white powders.

Fulminating Silver of Brugnatelli.—This curious and dangerous compound is prepared as follows:—100 grains of fused and finely powdered nitrate of silver are added to an ounce of warm alcohol, and the mixture stirred in a sufficiently large glass basin; an ounce of fuming nitric acid is then added, and presently a violent effervescence ensues; a powder falls; as soon as this appears white, cold water is added, and the powder is immediately to be collected upon a filter, washed, and carefully dried at a temperature of 100°. In collecting and handling this powder, the utmost caution is requisite; it should be made in small quantities only, and touched with nothing hard, for it has sometimes exploded upon the contact of a glass rod,

even under water: the feather of a common quill serves to collect it; and it should be kept in a wide-mouthed vessel covered by paper, and by no means in a stoppered or even a corked phial, as many serious accidents have arisen from its sudden and unexpected explosion. In short, one cannot be too careful in meddling with it; and its use for fulminating balls and for other purposes of amusement is highly dangerous. Liebeg's process for its preparation differs a little from the above, and is as follows:—A drachm of refined silver is dissolved in half an ounce of nitric acid, sp. grav. 1.52; two ounces of alcohol, sp. grav. 0.85, are then added, and the whole heated in a matrass; white flocculi soon appear, and when ebullition begins the heat is to be withdrawn; the effervescence, however, continues, and the powder falls; when action ceases, the powder is to be collected with the precautions above described. Fulminating silver thus obtained acquires a dingy hue by exposure to light; it dissolves in about 40 parts of boiling water, and as the solution cools, it is deposited in minute crystals. It detonates in the quantity of a grain, or even half a grain, with great violence, when heated, or touched by any hard body: placed upon a piece of rock crystal, and touched in the slightest manner by another crystal, it explodes violently; upon the contact of sulphuric acid, and by the electric spark, it also detonates. The nature of this substance has been investigated by Liebeg and Gay-Lussac (*Ann. de Chim. et Phys.* xxiv. and xxv.), who have shown that it is a compound of oxide of silver with an acid having the same composition as the cyanic acid, and that the above fulminating product is, therefore, strictly speaking, a *cyanate of silver*. But there are some peculiarities attending the arrangement of its elements, which require further explanation.

When, for instance, fulminating silver is digested in solution of potassa, a compound is obtained, which consists of two proportionals of cyanic acid, one of potassa, and one of oxide of silver, and a similar result is obtained with baryta and lime; these triple compounds are capable of crystallizing, and they possess detonating properties; so that a compound of two proportionals of cyanic acid and one of oxide of silver, appears to constitute an acid, which unites to alkaline bases, and forms detonating compounds. The fulminating compound

of silver is composed, according to Liebig and Gay-Lussac, of

1	proportional of cyanogen	=	26
1	"	oxygen	=	8
1	"	oxide of silver	=	118
									<hr/>
									152

and the detonating salt of potassa, of

2	proportionals of cyanic acid (34×2)	=	68
1	proportional of oxide of silver	=	118
1	"	potassa	=	48
									<hr/>
									234

Fulminating mercury is an analogous compound of protoxide of mercury and cyanic acid, and when decomposed by the fixed alkalis, the mercury constitutes a part of the triple detonating salt; and for mercury some other metals may be substituted. Cyanic acid in these peculiar states of combination has been called *fulminic acid*, but all attempts to obtain it in an insulated state have failed.

The soluble salts of silver are recognised by furnishing a white precipitate with muriatic acid, which blackens by exposure to light, and which is readily soluble in ammonia; and by affording metallic silver upon the immersion of a plate of copper. The salts insoluble in water are soluble in liquid ammonia, and when heated on charcoal before the blowpipe they afford a globule of silver.

Alloys of Silver.—The compounds of this metal with potassium and sodium have not been examined. It unites difficultly with iron, and does not combine with cobalt, except in very small proportions. It combines with manganese, and readily with arsenic.

When silver and steel are fused together, an alloy is formed, which appears perfect while in fusion, but globules of silver exude from it on cooling, which shows the weak attraction of the metals. At a very high temperature the greater part of the silver evaporates, but a portion equal to about 1 in 500 remains, forming a perfect alloy, admirably adapted to the formation of cutting instruments.—Stoddart and Faraday, on the Alloys of Steel, *Quarterly Journal*, ix.

Silver readily combines with zinc and tin, forming brittle alloys. The alloy of silver with copper is of the most import-

ance, as it constitutes plate and coin. By the addition of a small proportion of copper to silver, the metal is rendered harder and more sonorous, while its colour is scarcely impaired. The *standard silver* of this country consists of $11 \frac{2}{10}$ pure silver and $\frac{18}{10}$ copper, or 11.10 silver and 0.90 copper. A pound troy, therefore, is composed of 11 oz. 2 dwts. pure silver, and 18 dwts. of copper, and it is coined into 66 shillings.

With lead the alloy is grey and brittle, as also with antimony, bismuth, cobalt, and arsenic.

Amalgam of silver is sometimes employed for *plating*; it is applied to the surface of copper, and the mercury being evaporated by heat, the remaining silver is burnished. The better kind of plating, however, is performed by the application of a plate of silver to the surface of the copper, which is afterwards beaten or drawn out. A mixture of chloride of silver, chalk, and pearlash is employed for silvering brass: the metal is rendered very clean, and the above mixture, moistened with water, rubbed upon its surface. In this way thermometer scales and clock dials are usually silvered.

The analysis of alloyed silver is a very important process, and in continual practice by refiners and assayers. It may be performed in the humid way by dissolving the alloy in nitric acid, precipitating with muriatic acid, and either reducing the chloride by potassa in the way above described, or estimating the quantity of silver which it contains. The usual method, however, which is employed at the Mint, and by the refiners, is *cupellation*.

Of the useful metals, there are three only which are capable of resisting the action of air at high temperatures; these are silver, gold, and platinum; the others, under the same circumstances, become oxidized: it might, therefore, be supposed, that an alloy, containing one or more of the former metals, would suffer decomposition by mere exposure to heat and air, and that the oxidable metal would burn away. This, however, is not the case; for if the proportion of the latter be small, it is protected, as it were, by the former; or, in other cases, a film of oxide coats the fused globule, and prevents the further action of the air. These difficulties are overcome by adding to the alloy some highly oxidable metal, the oxide of

which is fusible. Lead is the metal usually selected for this purpose, though bismuth will also answer. Supposing, therefore, that an alloy of silver and copper is to be *assayed*, or analyzed by cupellation, the following is the mode of proceeding.

A clean piece of the metal, weighing about 30 grains, is laminated, and accurately weighed in a very sensible balance. It is then wrapped up in the requisite quantity of sheet lead, (pure and reduced from litharge,) and placed upon a small *cupel*, or shallow crucible, made of bone earth, which has been previously heated. The whole is then placed under the muffle, heated to bright redness; the metals melt, and by the action of the air which plays over the hot surface, the lead and copper are oxidized and absorbed by the cupel, and a button of pure silver ultimately remains, the completion of the process being judged of by the cessation of the oxidation and motion upon the surface of the globule, and by the very brilliant appearance assumed by the silver when the oxidation of its alloy ceases. The button of pure metal is then suffered to cool gradually, and its loss of weight will be equivalent to the weight of the alloy, which has been separated by oxidation.

To perform this process with accuracy, many precautions are requisite, and nothing but practice can teach these, so as to enable the operator to gain certain results. An excellent article upon the subject will be found in Aikin's *Chemical Dictionary*, and in Mr. Children's *Translation of Thenard on Chemical Analysis*.

Section XXX. GOLD.

GOLD occurs in nature in a metallic state, alloyed with a little silver or copper, and in this state is called *native gold*. Its colour is various shades of yellow; its forms are massive, ramose, and crystallized in cubes and octoëdra. The veins of gold are confined to primitive countries, but large quantities of this metal are collected in alluvial soils and in the beds of cer-

tain rivers, more especially those of the west coast of Africa, and of Peru, Brazil, and Mexico. In Europe, the streams of Hungary and Transylvania have afforded a respectable quantity of gold ; it has been found also in the Rhine, the Rhone, and the Danube. Small quantities have been collected in Cornwall, and in the county of Wicklow in Ireland.

Gold may be obtained pure by dissolving one part by weight of standard gold in three of nitro-muriatic acid, (composed of one part, by weight, of nitric, and two of muriatic acid,) evaporating the solution to dryness, (by a gentle heat towards the end of the process,) redissolving the dry mass in distilled water, filtering, and adding to it a solution of protosulphate of iron ; a black powder falls, which, after having been washed with dilute muriatic acid and distilled water, affords, on fusion, a button of pure gold. For the purpose of solution it may conveniently be kept in the pulverulent state.

Gold is of a deep yellow colour. It melts at a bright red heat, and when in fusion appears of a brilliant green colour. Its specific gravity is 19.3.

Gold is so malleable, that it may be extended into leaves which do not exceed $\frac{1}{300}$ of an inch in thickness. It is also very ductile. It shows no tendency to unite to oxygen when exposed to its action in a state of fusion ; but if an electric discharge be passed through a very fine wire of gold, a purple powder is produced, which has been considered as an oxide, though probably it is only finely divided gold.

Oxide of Gold may be obtained by adding a solution of potassa, not in excess, to a concentrated solution of muriate of gold ; the precipitate must be washed with water, and dried at a temperature of 100° ; if the heat exceed this, a portion of the oxide is reduced, and it is then only partially soluble in muriatic acid.

According to Pelletier, the best process for obtaining oxide of gold consists in the decomposition of the chloride by magnesia, washing the precipitate with dilute nitric acid, to remove any excess of the precipitant, and drying it at a very low heat. By the first process the oxide is obtained in the form of a yellow hydrate ; but when boiled in water, it becomes anhydrous, and of a deep brown tint. It is insoluble in water and is reduced to the metallic state by exposure to

light and by a moderate heat. At a red heat it is presently reduced. It dissolves readily in muriatic acid, and affords, upon evaporation, a chloride: it dissolves in sulphuric and nitric acids, but those solutions are decomposed when diluted, and yield no saline compound when evaporated with the utmost caution. These properties led Pelletier to examine the action of alkalis upon this oxide, and he found that, digested in a solution of caustic potassa, it was dissolved: it also combines with baryta, and in these cases apparently plays the part of a weak acid; it may, therefore, be called *auric acid*. Boiled with chloride of potassium or sodium, a yellow solution results, which is alkaline, and contains chloride of gold and aurate of potassa or soda. The action of ammonia on chloride of gold will presently be noticed.

There is much difficulty in determining the prime equivalent gold; for dissonant results are afforded by the analyses of its various compounds. The view generally adopted, but by no means satisfactorily established, is, that the above is a *tritoxide*, and as, according to the best analyses, it contains 10.77 *per cent.* of oxygen (Berzelius; and Javal, *Ann. de Chim. et Phys.* xvii.), it follows that the number 200 will represent the metal, and that the above oxide will consist of

1 proportional of gold	=	200
3 proportionals of oxygen (8 × 3)	=	24
							<hr/>
							224

A *protoxide* and a *deutoxide* of gold are by some admitted; the former by Berzelius, and the latter by Oberkampff; but they cannot be identified as distinct combinations, and they are not salifiable.

Chloride of Gold.—When gold in a state of minute division is heated in chlorine, a compound of a deep yellow colour results. Gold leaf also dissolves easily in a strong aqueous solution of chlorine, and affords a similar compound on evaporation. The common solvent of gold, however, for the purpose of obtaining the chloride, is the nitromuriatic acid, composed of two parts of muriatic and one of nitric acid. By evaporation, the saturated solution affords prismatic crystals of a deep orange colour, very deliquescent, and readily decomposed by heat, leaving a spongy mass of pure gold; it is said that a very

minute portion of the metal also passes off with the chlorine and water. When concentrated sulphuric acid is poured into a strong solution of this compound, it causes a precipitation of *anhydrous chloride of gold*.

The chloride of gold obtained by the careful evaporation of the nitromuriatic solution, appears, from such experiments as have been made upon it, to consist of one proportional of gold, and two of chlorine; but this result is at variance with others, and with the composition of the oxide; so that further experiments are required to determine the point and to remove the difficulties attendant on establishing the prime equivalent of gold.

When potassa is added to the solution of chloride of gold, the whole of the metal is not thrown down, a portion being retained so as to form a *triple chloride of gold and potassium*, which is very soluble, and not decomposed by further excess of alkali: it is on this account that a very acid solution of muriate of gold will afford no precipitate whatever with potassa or soda, the triple salt formed being in that case sufficient to employ the whole of the oxide of gold.

A *triple chloride of gold and sodium* may be obtained by dissolving 300 grains of gold in nitromuriatic acid, adding 19 grains of common salt, and evaporating the solution; yellow prismatic crystals are obtained, consisting, according to Thomson, of

1 proportional of deutochloride of gold	.	.	.	=	272
1 „ chloride of sodium	.	.	.	=	60
8 proportionals of water	.	.	.	=	72
					<hr/>
					404

When liquid ammonia is added to a concentrated solution of muriate of gold diluted with about three parts of water, a yellowish-brown precipitate is formed, which, if collected upon a filter, washed with a little water, and carefully dried at the temperature of 212° , is *fulminating gold*. Bergman first showed that this compound consists of about five parts of peroxide of gold and one of ammonia: when heated to about 400° , it explodes violently, the gold is reduced, and nitrogen and water are evolved; hence it appears that the ammonia is decomposed, that its hydrogen uniting with the oxygen of the oxide forms water, and that the nitrogen is suddenly liberated. It explodes by friction with hard bodies, and by an electrical

shock. If two or three grains be detonated upon a thin piece of platinum leaf, the metal is torn at the point of contact, as is the case with all these detonating compounds.

Muriate of gold is discoloured by steam in the same way, and apparently from the same cause, as nitrate of silver. (See page 183.) It is decomposed by phosphorus and charcoal, and by sulphurous acid: a piece of paper, moistened with it and exposed to light, also becomes purple in consequence of its decomposition. According to Van Mons, this solution of gold is decomposed by several vegetable acids, and when mixed with binoxalate of potassa, carbonic acid gas is evolved, and the gold gradually separated.

When solution of protosulphate of iron is added to muriate of gold, the mixture instantly acquires a dingy green or brown tinge, and appears of a beautiful green if viewed by strong transmitted light: these appearances depend upon the presence of an infinite number of small particles of gold in the metallic state, its oxygen having been imparted to the salt of iron; they soon subside in the form of a brown powder, which may be collected upon a filter, and with a little borax fused into a button. This method of separating gold from its solution is often convenient in analytical operations.

Protomuriate of tin, added to a dilute solution of chloride of gold, occasions an instant change of colour to a reddish-brown or dirty purple: if a piece of tin foil be immersed in a dilute solution of the chloride, the same purple powder is presently thrown down upon it: this powder is used in enamel painting, and for tingeing glass of a fine red colour, under the name of *purple of Cassius*: it is a compound of peroxide of tin and oxide of gold, the latter metal appearing to be in a very low state of oxidizement, and yet soluble in muriatic acid: it is also soluble in ammonia, forming a deep purple liquor. It would appear from Proust's experiments to consist of about three parts of oxide of tin, and one of oxide of gold. Oberkampff found the composition and colour of the precipitates formed by protomuriate of tin, in solutions of gold, liable to much variation. When the tin predominates, it is of a violet colour, but when the gold is in excess, it is more pink, and these colours are also communicated to enamel. Oberkampff and Macardieu state, that the gold in the compound is in the

metallic state ; that the violet combination contains 60 oxide of tin, and 40 gold ; and the pink about 20 and 80. (*Ann. de Chim. et Phys.* xxx. 147.)

When nitrate or sulphate of silver is added to muriate of gold, a precipitate falls, consisting of chloride of silver and oxide of gold ; the latter may be removed by muriatic acid.

If a solution of muriate of gold be mixed with sulphuric ether, it combines with the oxide, and an *ethereal solution of gold* is obtained. Polished steel dipped into this solution acquires a coat of gold, and it has hence been employed for gilding delicate cutting instruments.

According to Berzelius and Pelletier, a *protochloride of gold* is obtained by exposing the perchloride to a heat not exceeding that of melting tin ; it is of a yellow colour, and is not dissolved by water, but gradually converted into metallic gold and the perchloride.

Iodide of Gold.—The action of *iodine* on gold has been examined by M. Pelletier. (*Quarterly Journal of Science and Arts*, x. 121.) When hydriodate of potassa is added to muriate of gold, it produces a very copious yellowish brown precipitate, insoluble in cold water, and easily decomposed by heat, and by the liquid alkalis. When boiled in water, to deprive it of excess of iodine, it consists of

Iodine	34
Gold	66
						<hr/> 100

If this be considered a compound of one proportional of gold and one of iodine, the number 242 must be adopted as the representative of gold, a number so much at variance with that deduced from other experiments, as to show the necessity of further inquiries, before the equivalent of the metal can be satisfactorily determined.

Bromide of Gold.—Bromine combine with gold, and forms a dark gray substance, soluble in water, and crystallizing from its solution in deep brown crystals. This salt has so intense a colour, that it communicates a tinge to 5000 parts of water.

Sulphuret of Gold is procured by passing sulphuretted hydrogen through an aqueous solution of muriate of gold. It

is a black substance, consisting probably of 97 gold + 30 sulphur. (Oberkampff, *Ann. de Chim.* tom. lxxx.) These numbers seem to indicate one proportional of gold and three of sulphur.

Phosphuret of Gold is obtained by heating gold leaf with phosphorus, in a tube deprived of air. It is a gray substance of a metallic lustre, and consists probably of one proportional of gold and one of phosphorus. It is decomposed when heated under exposure to air.

Alloys of Gold.—A very curious detail of an extended and accurate series of experiments upon the alloys of gold has been published in the *Philosophical Transactions* for 1803, by Mr. Hatchett: his experiments were generally made with eleven parts of gold and one of alloy; or 38 grains of alloy to the ounce of gold.

The alloys of gold with potassium and sodium have not been examined. With *manganese* it forms a gray brittle alloy. With *iron* the alloy is malleable and ductile, and harder than gold; its colour dull white, and its specific gravity 16.885. The metals expand by union; so that, supposing their bulk before combination to have been 1000, after combination it is 1014.7. With *zinc* the compound is brittle and brass-coloured. Specific gravity 16.937. The metals contract a little in uniting, the original bulk being 1000, that of the alloy is 997. The brittleness continued when the zinc was reduced to $\frac{1}{60}$ of the alloy. The fumes of zinc in a furnace containing fused gold, make it brittle. *Tin* formed a whitish alloy, brittle, when thick, but flexible in thin pieces. Specific gravity 17.307. Bulk before fusion 1000; after fusion 981; so that there is considerable contraction. The old chemists called tin *diabolus metallorum*, from its property of rendering gold brittle, but Mr. Bingley's experiments quoted by Mr. Hatchett, show that $\frac{1}{60}$ of tin does not render gold brittle.

The alloy of *lead* is very brittle when that metal only constitutes $\frac{1}{1920}$ of the alloy; even the fumes of lead destroy the ductility of gold. The specific gravity is 18.080; and 1000 parts become 1005. A very remarkable fact in respect to this alloy is, that its specific gravity diminishes to a certain extent, as the proportion of lead diminishes, and is at its maximum when the lead amounts only to $\frac{1}{96}$ th part, the quantity of gold remaining the same, and the deficiency being made

up with copper. The following Table, drawn up by Mr. Hatchett, exhibits this remarkable fact :—

METALS.	Grains.	Sp. Gravity of Alloy.	Bulk before Union.	Bulk after Union.	Expansion.
Gold . . .	442	18.080	1000	1005	5
Lead . . .	38				
Gold . . .	442	17.765	1000	1005	6
Copper . .	19				
Lead . . .	19				
Gold . . .	442	17.312	1000	1022	22
Copper . .	30				
Lead . . .	8				
Gold . . .	442	17.032	1000	1035	35
Copper . .	34				
Lead . . .	4				
Gold . . .	442	16.627	1000	1057	57
Copper . .	37.5				
Lead . . .	0.5				
Gold . . .	442	17.039	1000	1031	31
Copper . .	37.75				
Lead . . .	0.75				

The alloy with *nickel* was of a brass colour and brittle. The specific gravity of the gold being 19.172, and of the nickel 7.8, that of the alloy was 17.068. An expansion had taken place, 1000 parts before fusion having become 1007. With *cobalt* the alloy was very brittle. Specific gravity 17.112. 1000 parts became 1001 after fusion. With *bismuth* the alloy was of a brass colour, very brittle, and of a specific gravity = 18.038. 1000 parts became 988 after fusion, so that the condensation was considerable. When the bismuth amounted only to $\frac{1}{1920}$ th part, the alloy was still brittle, though the colour was nearly that of gold.

With *copper* (*standard gold*) the alloy is perfectly ductile and malleable, but harder than pure gold, and resists wear better than any other alloy except that with silver. Its specific gravity is 17.157. Gold coin is an alloy of eleven parts of gold and one of copper; of this alloy, 20 troy pounds are coined into 934 sovereigns and one half-sovereign; one pound formerly was coined into $44\frac{1}{2}$ guineas; it now produces $46\frac{2}{3}$ sovereigns.

Arsenic and *antimony*, when alloyed in very small proportions with gold, destroy its colour and render it quite brittle.

The analysis of most of the alloys of gold is performed by cupellation. The triple alloy of gold, silver, and copper, may be analyzed by digesting it in nitric acid, which takes up the silver and copper, and leaves the gold in the form of a black powder, which may be fused into a button, and weighed. The silver may be thrown down in the state of chloride by solution of common salt, and the copper precipitated by iron.

The *assay of gold* is more complicated than that of silver, in consequence of the high attraction which it has for copper, and which prevents its complete separation by mere cupellation. An alloy, therefore, of copper with gold is combined with a certain quantity of silver, previous to cupellation; this is then cupelled with lead in the usual way, and the silver is afterwards separated by the action of nitric acid.

The real quantity of gold or silver taken for an assay is very small; from 18 to 36 grains, for instance, for silver, and from 6 to 12 for gold; whatever the quantity may be it is called the *assay pound*. The silver assay pound is divided into 12 ounces, and each ounce into 20 penny-weights. The gold assay pound is subdivided into 24 carats, and each carat into 4 assay grains.—Aikin's *Dictionary*, Art. ASSAY.

Mercury and gold combine with great ease, and produce a white amalgam, much used in gilding. For this purpose the amalgam is applied to the surface of the silver; the mercury is then driven off by heat, and the gold remains adhering to the silver, and is burnished. This process is called *water gilding*.

In gilding porcelain, *gold powder* is generally employed, obtained by the decomposition of the muriate; it is applied

with a pencil, and burnished after it has been exposed to the heat of the porcelain furnace.

Many curious facts relating to the properties of gold, and its uses in the arts, will be found in Dr. Lewis's *Philosophical Commerce of the Arts*.

Section XXXI. PLATINUM.

THIS metal, in the metallic state, is found in small grains in South America, confined to alluvial strata chiefly in Brazil and Peru. It has also been found in the province of Antioquia in North America, and in considerable quantities in the Uralian mountains of Siberia. These grains, besides platinum, contain generally gold, iron, lead, palladium, rhodium, iridium, and osmium, and often oxide of titanium and chromate of iron.

The pure metal * may be obtained by dissolving crude platinum in nitro-muriatic acid, and precipitating by a solution of muriate of ammonia. The first precipitate is heated, dissolved in nitro-muriatic acid, and again precipitated as before. The second precipitate is heated white hot, and pure platinum remains. It is a white metal, extremely difficult of fusion, and unaltered by the joint action of heat and air. The following details of the mode of rendering platinum malleable, I transcribe from Dr. Wollaston's latest paper upon this subject published in the *Philosophical Transactions* for 1829.

“The usual means of giving chemical purity to this metal, by solution in aqua regia and precipitation with sal ammoniac, are known to every chemist; but I doubt whether sufficient care is usually taken to avoid dissolving the iridium contained in the ore, by due dilution of the solvent. In an account which I gave in the *Philosophical Transactions* for 1804, of a new metal, Rhodium, contained in crude platina, I have mentioned this precaution, but omitted to state to what degree the acids

* The method followed in Paris for obtaining pure platinum is described at length by M. Baruel in the 12th volume of the *Quarterly Journal of Science, O.S.*

should be diluted. I now, therefore, recommend, that to every measure of the strongest muriatic acid employed, there be added an equal measure of water; and, moreover, that the nitric acid used be what is called ‘single aquafortis;’ as well for the sake of obtaining a purer result, as of economy in the purchase of nitric acid.

“With regard to the proportions in which the acids are to be used, I may say, in round numbers, that muriatic acid, equivalent to 150 marble, together with nitric acid equivalent to 40 marble, will take 100 of crude platina; but in order to avoid waste of acid, and also to render the solution purer, there should be in the menstruum a redundancy of 20 *per cent.* at least of the ore. The acids should be allowed to digest three or four days, with a heat which ought gradually to be raised. The solution, being then poured off, should be suffered to stand until a quantity of fine pulverulent ore of iridium, suspended in the liquid, has completely subsided; and should then be mixed with 41 parts of sal ammoniac, dissolved in about five times their weight of water. The first precipitate, which will thus be obtained, will weigh about 165 parts, and will yield about 66 parts of pure platina.

“As the mother-liquor will still contain about 11 parts of platina, these, with some of the other metals yet held in solution, are to be recovered, by precipitation from the liquor with clean bars of iron, and the precipitate is to be redissolved in a proportionate quantity of aqua regia, similar in its composition to that above directed to be used: but in this case, before adding sal-ammoniac, about one part by measure of strong muriatic acid should be mixed with 32 parts by measure of the nitro-muriatic solution, to prevent any precipitation of palladium or lead along with the ammonio-muriate of platina.

“The yellow precipitate must be well washed, in order to free it from the various impurities which are known to be contained in the complicated ore in question; and must ultimately be well pressed, in order to remove the last remnant of the washings. It is next to be heated, with the utmost caution, in a black-lead pot, with so low a heat as just to expel the whole of the sal-ammoniac, and to occasion the particles of platina to cohere as little as possible; for on this depends the ultimate ductility of the product.

“The gray product of platina, when turned out of the crucible, if prepared with due caution, will be found lightly coherent, and must then be rubbed between the hands of the operator, in order to procure, by the gentlest means, as much as can possibly be so obtained, of metallic powder, so fine as to pass through a fine lawn sieve. The coarser parts are then to be ground in a wooden bowl with a wooden pestle, but on no account with any harder material, capable of burnishing the particles of platina *; since every degree of burnishing will prevent the particles from cohering in the further stages of the process. Since the whole will require to be well washed in clean water, the operator, in the later stages of grinding, will find his work much facilitated by the addition of water, in order to remove the finer portions, as soon as they are sufficiently reduced to be suspended in it.

“Those who would view this subject scientifically should here consider, that as platina cannot be fused by the utmost heat of our furnaces, and consequently cannot be freed, like other metals, from its impurities, during igneous fusion, by fluxes, nor be rendered homogeneous by liquefaction, the mechanical diffusion through water should here be made to answer, as far as may be, the purposes of melting; in allowing earthy matters to come to the surface by their superior lightness, and in making the solvent powers of water effect, as far as possible, the purifying powers of borax and other fluxes in removing soluble oxides.

“By repeated washing, shaking, and decanting, the finer parts of the gray powder of platina may be obtained as pure † as other metals are rendered by the various processes of ordinary metallurgy; and, if now poured over, and allowed to subside

* “The following experiment will prove the necessity of attending to this precaution:—if a wire of platina be divided with a sharp tool in a slanting direction, and, being then heated to redness, be struck upon an anvil with a hammer, so as to force into contact the two newly-divided surfaces, they will become firmly welded together; but if the surfaces have previously been burnished with any hard substance, the welding will be effected, if at all, with very great difficulty.

“When the powder of platina has been over-heated in decomposing the ammonio-muriate, or has been burnished in the grinding, I have in vain endeavoured to give it a welding surface, by steeping it in a solution of sal-ammoniac in nitric acid.”

† “Sulphuric acid, digested upon the gray powder of platina, thus purified, extracted less than $\frac{1}{1000}$ th part of iron.”

in a clean basin, a uniform mud or pulp will be obtained, ready for the further process of casting.

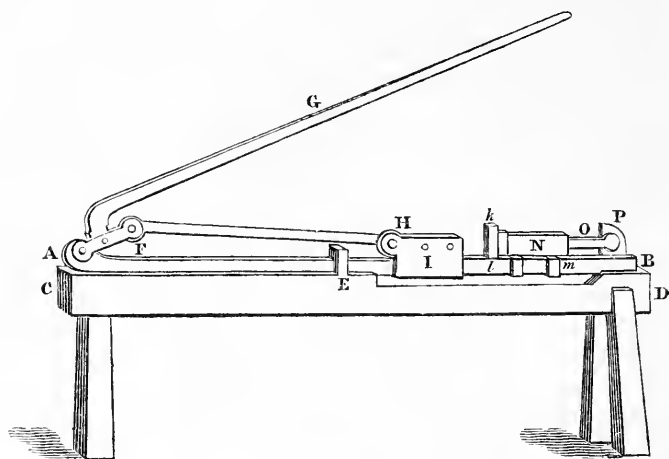
“The mould which I have used for casting is a brass barrel, $6\frac{3}{4}$ inches long, turned rather taper within, with a view to facilitate the extraction of the ingot to be formed, being 1.12 inches in diameter at top, and 1.23 inches at a quarter of an inch from the bottom, and plugged at its larger extremity with a stopper of steel, that enters the barrel to the depth of a quarter of an inch. The inside of the mould being now well greased with a little lard, and the stopper being fitted tight into the barrel by surrounding it with blotting paper, (for the paper facilitates the extraction of the stopper, and allows the escape of water during compression,) the barrel is to be set upright in a jug of water, and is itself to be filled with that fluid. It is next to be filled quite full with the mud of platina; which, subsiding to the bottom of the water, is sure to fill the barrel without cavities, and with uniformity,—a uniformity to be rendered perfect by subsequent pressure. In order, however, to guard effectually against cavities, the barrel may be weighed after filling it, and the actual weight of its contents being thus ascertained, may be compared with that weight of platina and water which it is known by estimate that the barrel ought to contain*. A circular piece of soft paper first, and then of woollen cloth, being laid upon the surface, allow the water to pass, during partial compression by the force of the hand with a wooden plug. A circular plate of copper is then placed upon the top, and thus sufficient consistency is given to the contents to allow of the barrel being laid horizontally in a forcible press.

“The press which I have generally used for this purpose (Plate I.) consists of a flat iron bar AB, set edgewise, and

* “From the mean weight of the ingots obtained in previous operations, it is known that the barrel described in the text ought to contain 16 ounces troy of dry platina powder. The weight of the contents of the barrel = 16 ounces \times sp. grav. of platina — 1

sp. grav. of platina + the weight of a cubic inch of water \times capacity of the barrel in cubic inches = 16 ounces $\times \frac{20.25}{21.25} + .526$ ounces $\times 7.05 = 18.9575$ ounces troy. Should the contents of the barrel weigh materially less than this estimated weight, there must be a want of uniformity in the disposition of the powder within the barrel.”

screwed down by a hook E, near its middle, where it would otherwise be liable to bend, to a strong wooden bench C D. The bar is connected by a pivot at its extremity A, with the lever A F G. An iron rod F H, which turns at its two extremities upon the pivots F and H, proceeds from the lever at F,



and, as the lever descends, propels forward the carriage I, which slides along the bar. A stopper or block being placed in the vacant space I k, the carriage communicates motion to the cradle k l m, which is also made to slide along the bar, and carries the barrel N, which lies upon the cradle, straight against the piston O, which rests by its end against P, a projection in the further extremity of the bar.

“ The weight, which in this machine, when the angle of the lever’s elevation is small, will keep the power, applied vertically at the extremity of the lever, *in equilibrio* = that power $\times \frac{AG \times FH}{AF [AF + FH]}$ \times cotan of the angle of the lever’s elevation ; which expression, in the case of the press actually used, becomes, Power $\times 5$. cotan of the angle of the lever’s elevation. This expression, at an elevation of 5° , becomes nearly $60 \times$ power, and at an elevation of 1° , becomes nearly $300 \times$ power ; and when the lever becomes horizontal, the multiplier of the power becomes *quasi* infinite. This expla-

nation will be sufficient to show the mechanical advantage with which, by means of this press, the weight of the operator, acting on the end of the lever, will be made to bear against the area of the section of the barrel, a circle little more than an inch in diameter.

“ After compression, which is to be carried to the utmost limit possible, the stopper at the extremity being taken out, the cake of platina will easily be removed, owing to the conical form of the barrel ; and being now so hard and firm that it may be handled without danger of breaking, it is to be placed upon a charcoal fire, and there heated to redness, in order to drive off moisture, burn off grease, and give to it a firmer degree of cohesion.

“ The cake is next to be heated in a wind-furnace ; and for this purpose is to be raised upon an earthen stand about $2\frac{1}{2}$ inches above the grate of the furnace, the stand being strown over with a layer of clean quartzose sand, on which the cake is to be placed, standing upright on one of its ends. It is then to be covered with an inverted cylindrical pot, of the most refractory crucible ware, resting at its open end upon the layer of sand ; and care is to be taken that the sides of the pot do not touch the cake.

“ To prevent the blistering of the platina by heat, which is the usual defect of this metal in its manufactured state, it is essential to expose the cake to the most intense heat that a wind-furnace can be made to receive, more intense than the platina can well be required to bear under any subsequent treatment ; so that all impurities may be totally driven off, which any lower temperature might otherwise render volatile. The furnace is to be fed with Staffordshire coke, and the action of the fire is to be continued for about twenty minutes from the time of lighting it, a breathing heat being maintained during the last four or five minutes.

“ The cake is now to be removed from the furnace, and being placed upright upon an anvil, is to be struck, while hot, on the top, with a heavy hammer, so as at one heating effectually to close the metal. If in this process of forging the cylinder should become bent, it should on no account be hammered on the side, by which treatment it would be cracked irremediably ; but must be straightened by blows upon the

extremities, dexterously directed, so as to reduce to a straight line the parts which project.

“The work of the operator is now so far complete, that the ingot of platina may be reduced, by the processes of heating and forging, like that of any other metal, to any form that may be required. After forging, the ingot is to be cleaned from the ferruginous scales which its surface is apt to contract in the fire, by smearing over its surface with a moistened mixture of equal parts by measure of crystallized borax and common salt of tartar, which, when in fusion, is a ready solvent of such impurities*, and then exposing it, upon a platina tray, under an inverted pot, to the heat of a wind-furnace. The ingot, on being taken out of the furnace, is immediately to be plunged into dilute sulphuric acid, which in the course of a few hours will entirely dissolve the flux adhering to the surface. The ingot may then be flattened into leaf, drawn into wire, or submitted to any of the processes of which the most ductile metals are capable.

“The perfection of the methods above described, for giving to platina complete malleability, will best be estimated by comparing the metal thus obtained, in respect of its specific gravity, with platina, which has undergone complete fusion; and by comparing it, in respect of its tenacity, with other metals possessing that quality in the greatest perfection.

“The specific gravity of platina, drawn into fine wire, from a button which had been completely fused by the late Dr. E. D. Clarke, with an oxy-hydrogen blowpipe, I found to be 21.16. The aggregate specific gravity of the cake of metallic mud, when first introduced into the barrel, exclusively of moisture, is about 4.3; when taken from the press, is about 10. That of the cake fully contracted, on being taken out of

*“The chemist will find this flux very serviceable for removing from his crucible or other vessels of platina those ferruginous scales with which, after long use, and particularly after being strongly heated in a coal or coke fire, they become incrustated. In the analysis of earthy minerals, I have been in the habit of using a similar flux, composed of two parts by weight of crystallized carbonate of soda, and one of crystallized borax, well ground together. It has the advantage of not acting, like caustic alkali, upon the platina crucible, and is a powerful solvent of jargon and many other minerals, which yield with difficulty to other fluxes. If the mineral to be operated on requires oxidation, in order to decompose it, a little nitre or nitrate of soda may be added.”

the wind-furnace before forging, is from 17 to 17.7. The mean specific gravity of the platina, after forging, is about 21.25, although that of some rods, after being drawn, is 21.4: but that of fine platina wire, determined by comparing the weight of a given length of it with the weight of an equal length of gold wire drawn through the same hole, I find to be 21.5, which is the maximum specific gravity that we can well expect to be given to platina.

“The mean tenacity, determined by the weights required to break them, of two fine platina wires, the one of $\frac{1}{30.000}$, the other of $\frac{1}{38.500}$ of an inch in diameter, reduced to the standard of a wire $\frac{1}{10}$ th of an inch in diameter, I found to be 409 pounds; and the mean tenacity of eleven wires, beginning with $\frac{1}{45.000}$ and ending with $\frac{1}{25.000}$ of an inch, reduced to the former standard, I found to be 589 pounds; the maximum of these eleven cases being 645 pounds, and the minimum 480 pounds. The coarsest and the finest wire which I tried present exceptions, since a wire of $\frac{1}{15.000}$ of an inch gave 290 pounds, and a wire of $\frac{1}{30.000}$ of an inch, 190 pounds. If we take 590 pounds, as determined by the eleven consecutive trials, to be the measure of the tenacity of the platina prepared by the processes above described, and consider that the tenacity of gold wire, reduced to the same standard, is about 500, and that of iron wire 600, we shall have full reason to be satisfied with the processes above detailed, by which platina has been rendered malleable.”

Platinum and Oxygen.—When nitrate of mercury is added to a dilute solution of muriate of platinum, a powder falls, which, when carefully heated, gives off calomel, and leaves a *black oxide of platinum*, composed, according to Mr. Cooper, of 100 platinum, + 4.5 oxygen.—(*Journal of Science and the Arts*, vol. iii.) It forms the base of an excellent black enamel.

When protochloride of platinum is gently heated in a solution of caustic potassa, a black oxide is formed, part of which is dissolved by the alkali, and part precipitated: it may be thrown down from its alkaline solution by dilute sulphuric acid. Heated in a retort, it is reduced with the escape of water and oxygen gas. It slowly dissolves in the acids, most of which decompose it and resolve it into peroxide and metal. According to Berzelius, this is the protoxide of platinum, and

if the number 96 be assumed as the equivalent of the metal, it will consist of

1	proportional of platinum	=	96
1	„ oxygen	=	8
							<hr/>
							104

When spongy platinum is heated to redness in an open vessel with caustic potassa, and the product when cold washed with water, a grey powder is obtained, which is partly dissolved by the alkali: the residue washed with dilute nitric acid, and afterwards with water, is a *sesquioxide* of platinum, consisting of

1	proportional of platinum	=	96
1½	„ oxygen	=	12
							<hr/>
							108

When sulphuret of platinum is digested in nitric acid, and carefully evaporated, or when perchloride of platinum is gently heated in sulphuric acid, a dark brown solution of *persulphate of platinum* is obtained: if this solution be mixed with nitrate of baryta, sulphate of baryta is thrown down, and pernitrate of platinum remains dissolved; this may be in part decomposed by solution of caustic soda, which forms a yellow precipitate, becoming brown when carefully washed and dried, and which is *hydrated peroxide* of platinum. Heated in a retort, it first gives out oxygen and becomes black; at a higher temperature it evolves oxygen, and the metal is reduced: it has a very feeble attraction for the acids, but readily combines with many of the salifiable bases; it dissolves in the caustic and carbonated alkalis, and may be combined with lime, strontia, and baryta, by adding those earths to its acid solution, when it falls in union with them in the form of a yellow powder. (Berzelius.) This oxide consists of

1	proportional of platinum	=	96
2	proportionals of oxygen (8 × 2)	=	16
							<hr/>
							112

Chlorides of Platinum.—When perchloride of platinum is exposed in a porcelain capsule to a temperature not exceeding that of melting tin, it is converted into a grey powder, insoluble in water, and not decomposed by sulphuric or nitric acids. It dissolves in boiling muriatic acid, and is decomposed,

as above stated, by caustic alkali, which separates protoxide. It is decomposed at a red heat, and only gives out chlorine without a trace of water. It is composed of

1 proportional of platinum	=	96
1 „ chlorine	=	36
						<hr/>
						132

It is, therefore, a *protochloride of platinum*.

When the solution of pure platinum in nitro-muriatic acid is evaporated, it affords a brown saline mass, which becomes deeper coloured upon the expulsion of its combined water. It is then a *perchloride of platinum*, yielding a yellow-brown solution in water, and easily soluble in alcohol. The latter solution is a useful re-agent to detect the presence of potassa: the salt, the base of which is to be ascertained, is dissolved in the smallest possible quantity of water, and mixed with the alcoholic solution of the perchloride: if it be potassa, a triple salt, insoluble in alcohol, is thrown down; if not, the liquid remains clear. (Berzelius.) This perchloride consists of

1 proportional of platinum	=	96
2 proportionals of chlorine (36 × 2)	=	72
						<hr/>
						168

Nitro-muriate of Platinum.—Nitro-muriatic acid is the readiest solvent of platinum. The solution affords crystals which are very deliquescent and acid, of hydrated perchloride or *permuriate of platinum*. The solution of this compound is distinguished from other metallic solutions by affording a precipitate upon the addition of muriate of ammonia, which is an *ammonio-muriate of platinum*, which, when carefully dried, consists of

1 proportional of perchloride of platinum	=	168
1 „ muriate of ammonia	=	54
						<hr/>
						222

When this ammonio-muriate is heated, it loses a little water and a portion of its muriate of ammonia, the remainder being decomposed by the chlorine, and resolved into nitrogen and muriatic acid. The platinum remains in the peculiar spongy state above referred to, and possessed of the singular power of determining the union of hydrogen and certain other inflammable gases with oxygen, originally discovered by Dober-

einer, and more fully explained in the section on Hydrogen (vol. i. p. 171).

The yellow precipitate occasioned by mixing chloride of potassium with perchloride of platinum, is a *triple chloride of platinum and potassium*. It is very sparingly soluble in water and dilute acids, and insoluble in alcohol. It consists of

1	proportional of perchloride of platinum . . .	= 168
1	„ chloride of potassium . . .	= 84
		<hr/> 252

With soda, perchloride of platinum forms a soluble compound, which is best obtained by adding to nitric acid in a retort, platinum with twice its weight of common salt, and applying heat till about four-fifths of the fluid have distilled over. The remaining liquor affords yellowish-brown prismatic crystals of the triple salt, which, exclusive of water of crystallization, consists of one proportional of perchloride of platinum, and one of chloride of sodium.

Ferrocyanate of potassa affords no precipitate in solution of muriate of platinum. Ether separates the platinum from the solution of the perchloride in the same way as it separates gold. Muriate of tin occasions a very characteristic red precipitate in very dilute solution of platinum. Sulphate of iron forms no precipitate, but tincture of galls throws down a dark green powder, which becomes pale on standing: the action of these re-agents is, however, rendered equivocal by the varying acidity of the solution.

Sulphurets of Platinum.—There are, according to E. Davy, three *sulphurets of platinum*. The first, formed by heating the finely-divided metal with sulphur; the second, by precipitating nitro-muriate of platinum by sulphuretted hydrogen; and the third, by heating three parts of the ammonio-muriate with two of sulphur. When sulphur and ammonio-muriate of platinum are mixed and heated in a small retort, a grey pulverulent bisulphuret of platinum is formed, which, by careful application of heat, loses half its sulphur. When the nitromuriatic solution of platinum is mixed with bihydrosulphuret of potassa or ammonia, a black powder falls, which Vauquelin considered as a hydrosulphuretted oxide, but which, when carefully dried over sulphuric acid in an exhausted receiver, yields,

according to Berzelius, no traces of water. When this precipitate is exposed upon paper to dry in the air, the sulphur absorbs oxygen, and becomes sulphuric acid, which chars the paper. When sulphuretted hydrogen is passed through solution of nitromuriate of platinum, the precipitate which falls consists of chloride and sulphuret of platinum. The sulphuret consists of one proportional of platinum and one of sulphur, and the bisulphuret of one and two; so that the sulphurets correspond in composition with the oxides.

Phosphurets of Platinum.—According to E. Davy, there are two phosphurets. The first, obtained by heating phosphorus with the metal; the second, by heating phosphorus with the ammonio-muriate of platinum. Platinum crucibles are easily injured by the phosphorus evolved during the decomposition of phosphoric salts.

Salts of Platinum.—The salts of platinum have been but little examined. Proust and Davy have described a *sulphate*, obtained by acidifying the sulphur in the sulphuret by means of nitric acid. It is of a brown colour, and very soluble in water, alcohol, and ether; and with soda, potassa, and ammonia, it forms triple salts. It consists of

26.3 sulphuric acid
73.7 peroxide of platinum.

Sulphate of platinum is a very delicate test of the presence of gelatine.

E. Davy found that the precipitate from solution of sulphate of platinum by a slight excess of ammonia, when boiled in potassa, washed and dried, was a *fulminating platinum*; it explodes at about 420° , with a loud report, and appears to be a compound of oxide of platinum, ammonia, and water.—*Phil. Trans.* 1817. He has also described a very singular compound of platinum (*Phil. Trans.* 1820, p. 108), obtained by mixing equal volumes of strong aqueous solution of the sulphate and of alcohol. The colour of the sulphate slowly disappears, and in some days a black substance subsides, which is washed and dried. It is also formed by boiling the sulphate and alcohol together for a few minutes. This substance is permanent in the air and insoluble in water. It detonates feebly when heated, and is not affected by chlorine, nor by nitric, sulphuric, and phosphoric acids; but it is slowly

soluble in muriatic acid. Put into liquid ammonia, it acquires fulminating properties; and plunged into ammoniacal gas it becomes red hot: the same phenomenon is exhibited by exposing it to the vapour of alcohol, or by placing it upon a piece of paper moistened with that fluid: in these cases the platinum is reduced with the evolution of heat, and the ignition seems to depend upon the slow combustion of the vapour of the alcohol. From Mr. Davy's analysis of this compound, it appears to contain 96.25 platinum, 0.12 oxygen, 0.0106 carbon, 3.6194 nitric acid and water; the acid being derived from the mode of preparing the sulphate. The phenomena exhibited by platinum in this state resemble those observed by Dobereiner as appertaining to spongy platinum.

The Alloys of Platinum have not been applied to any useful purposes. By combining 7 parts of platinum with 16 of copper and 1 of zinc, Mr. Cooper obtained a mixture much resembling gold.—(*Journal of Science and Arts*, vol. iii. p. 119.) Hermbstadt obtained a gold colour by combining 16 parts of platinum with 7 of copper and 1 of zinc.

Zinc, bismuth, tin, and arsenic, readily combine with platinum, and form fusible alloys. It also unites, though less readily, with copper, lead, and iron. It combines with gold, and unless there be great excess of the latter, the colour of the alloy resembles platinum.

If a small piece of tin, zinc, or antimony, be rolled up in platinum leaf, and exposed to the jet of a blowpipe, the two metals combine with such energy, when nearly white hot, as to produce a kind of explosion. Iron and steel also remarkably increase the fusibility of platinum.

The alloys of steel and platinum have been examined by Stodart and Faraday. They combine in all proportions, but from 1 to 3 *per cent.* of platinum appears best adapted for cutting instruments. Equal weights of the two metals produce a fine hard and brilliant alloy, of a specific gravity of 9.862; it appears well adapted for mirrors, for it takes a fine polish and does not tarnish. An alloy of 90 platinum and 20 steel has a specific gravity of 15.88.

The alloy of cobalt and platinum is fusible. With its weight of nickel, platinum forms a pale yellow alloy susceptible of a high polish, and obedient to the magnet. Mercury does not act upon manufactured platinum, but it combines with it

in the state of very fine division, in which it is obtained by heating the ammonio-muriate of platinum, and forms a buttery amalgam, which gradually hardens. When fused with silver in the proportion of 7 *per cent.* and upwards, it impairs the malleability and colour of the latter metal. This alloy is soluble in nitric acid; so that, if an alloy of gold and platinum be fused with silver, rolled into a plate, and digested in nitric acid, both the silver and platinum are dissolved.

Platinum has the property of being united by welding, either one piece to another, or with iron, or steel. Wires of steel and platinum, when welded and polished, exhibit a curious and beautiful surface, especially when the steel parts are slightly acted upon by dilute acid. This welding property of platinum may be usefully applied in the arts; rings may be joined so as to form a chain, the durability of which must add to its value; and with a view to economy, platinum may be joined to iron or steel for many uses in the laboratory of the chemist.

The perfection with which vessels of platinum resist the action of heat and air, of most of the acids, and of sulphur and mercury, render them peculiarly valuable in many of their applications: but its high value is against its very general adoption, for, although much cheaper than gold, it is worth between four and five times its weight of silver. Berzelius observes (*Lehrbuch*), that in the employment of platinum vessels, the following precautions must be attended to:—

1. They must not be subjected to the action of compounds which evolve chlorine.
2. Nitre and the alkalis must not be fused in them.
3. No metallic reductions must be performed in them, nor compounds of phosphorus decomposed so as to evolve that substance.
4. When metallic oxides are heated in a platinum crucible, the heat must not be raised beyond redness, provided the oxide is easily decomposed: hence the caution requisite with the oxides of lead, bismuth, copper, cobalt, nickel, and antimony, which, though they may not effect the fusion of the crucible, spoil it by their action upon its interior surface, which is rendered rough and porous.
5. That the immediate contact of the fuel (charcoal should always be used) with the crucible should be avoided as much as possible, especially at very high temperatures; for it is

thus, in process of time, rendered brittle and unsound. Small holes and fissures may be filled up and soldered with pure gold, but in that case the vessel must not be exposed to a white heat, because then the gold and platinum combine.

Section XXXII. OSMIUM.

OSMIUM, and the metals described in the three following sections, are contained in the ore of platinum. (See PLATINUM.) This ore is digested in nitro-muriatic acid, by which the greater portion is dissolved, and there remains a black powder, consisting chiefly of iridium and osmium, which, when fused with potassa and washed, furnishes a yellow alkaline solution of oxide of osmium. Saturate the alkali with sulphuric acid, pour the mixture into a retort, and distil. A colourless solution of the *oxide of osmium* passes into the receiver; it has a sweetish taste and a very peculiar smell, something like that of new bread: hence the application of the name *Osmium*. When mercury is shaken with this solution it becomes an amalgam, which is decomposed by distillation, and pure osmium remains.

To obtain the oxide of osmium in a pure, solid, and crystallized state, grind together, and introduce, when ground, into a cold crucible, three parts by weight of the pulverulent ore of iridium and one part of nitre. The crucible is to be heated to a good red in an open fire, until the ingredients are reduced to a pasty state, when osmic fumes will be found to arise from it. The soluble parts of the mixture are then to be dissolved in the smallest quantity of water necessary for the purpose, and the liquor thus obtained is to be mixed in a retort, with so much sulphuric acid, diluted with its weight of water, as is equivalent to the potash contained in the nitre employed; but no inconvenience will result from using an excess of sulphuric acid. By distilling rapidly into a clean receiver, for so long a time as the osmic fumes continue to come over, the oxide will be collected in the form of a white crust on the sides of the receiver, and these melting, it will run

down in drops beneath the watery solution, forming a fluid flattened globule at the bottom. When the receiver has become quite cold, the oxide will become solid and crystalline. One such operation has yielded 30 grains of the crystallized oxide, besides a strong aqueous solution of it.

Osmium was discovered by Tennant in 1803. (*Phil. Trans.*) It has a dark grey colour, and is not volatile when heated in close vessels; but heated in the air it absorbs oxygen, and forms a volatile oxide: it has not been fused. The aqueous solution of its oxide leaves a black spot when applied to the skin; it is decomposed, and metallic osmium thrown down by all the metals except gold, platinum, rhodium, and iridium. In this state of recent precipitation, it is somewhat soluble in nitric acid, but it produces no definite saline compounds with the acids. Alcohol and ether also partially reduce the oxide of osmium. The leading characters of osmium are its insolubility in the acids after it has been heated, its ready solubility in potassa, the facility with which it is oxidized, the singular smell of its oxide, its great volatility, and the purple or blue colour produced in its solution by tincture of galls, which is an extremely delicate and characteristic test of its presence.

Chloride of Osmium is a yellowish fuming liquid, obtained by passing chlorine over the metal. It readily dissolves in water, and may be distilled in close vessels without change.

When osmium is mixed with iodine, and heated, the latter passes off unaltered; so that probably they do not combine.

The other compounds of osmium have scarcely been examined.

Section XXXIII. IRIDIUM.

THIS metal was discovered at the same time as osmium, by Mr. Tennant: the various colours exhibited by the muriatic solution of its oxide suggested its name. The black powder which remains after native platinum has been digested in nitro-muriatic acid, consists chiefly of iridium and osmium; titanium and chromate of iron also occur in it. To obtain

iridium, this powder is fused in a silver crucible with twice its weight of hydrate of potassa for the space of an hour or more, the residue is washed, and the remaining insoluble portion is iridium, which has been oxidized by the process of fusion. This oxide is soluble in muriatic acid, and the solution is blue if free from iron, which communicates more or less of a green tint: when heated with the addition of a little nitric acid, it becomes red, probably in consequence of the peroxidizement of the iridium. When the muriatic solution of iridium is evaporated, it furnishes brown crystals, which are decomposed by a red heat, and leave finely-divided metallic iridium. They form a reddish-brown solution with water, which, if concentrated and mixed with a saturated solution of muriate of ammonia, afford a dark brown precipitate of the *ammonio-muriate of iridium*. The solution of the muriate is decomposed by all the metals except gold and platinum, and metallic iridium precipitated.

Iridium, obtained by immersing a plate of zinc into a solution of the muriate, or by violently heating that salt, is of a whitish colour, and, according to Mr. Children, who succeeded in fusing it by means of his large Voltaic apparatus, its specific gravity is above 18. Its most marked character is extremely difficult solubility in the acids: indeed, when pure, it is probably insoluble, although, when alloyed with platinum, a little is taken up by nitro-muriatic acid.

Oxides of Iridium.—These and the other compounds of this metal have been very little examined. The action of potassa or of nitre at a red heat is the only mode of oxidizing iridium. When sulphuretted hydrogen is passed into a solution of muriate of iridium it becomes colourless, but the metal remains in solution. The oxide of iridium, obtained by fusion with potassa, furnishes blue solutions; according to Vauquelin, it combines with bases: he suspects that it is the source of the blue of the sapphire, in combination with alumina. When the blue solution is boiled with nitric acid, it becomes red; in this state it gives the dark colour to the nitro-muriatic solution of crude platinum. These facts lead us to suspect that iridium is susceptible of three degrees of oxidizement; that the solutions of the protoxide are colourless; those of the deutoxide blue; and of the peroxide red.

When the ammonio-muriate of iridium is heated with sulphur, a black compound is obtained, containing, according to Vauquelin, 25 *per cent.* of sulphur and 75 of iridium. Iridium alloyed with lead, tin, copper, and silver, does not destroy the malleability of those metals. Berzelius observes, that iridium, combined in small quantities with platinum, adds to the valuable properties of the latter metal for the manufacture of crucibles, which are less easily acted upon by several agents than those of platinum perfectly pure.

In crude platinum, Dr. Wollaston discovered some flat white grains which resisted the action of the acids, and which he ascertained to consist of *a native alloy of osmium and iridium.*

We are as yet unacquainted with the equivalent numbers of osmium and of iridium.

Section XXXIV. RHODIUM.

RHODIUM and Palladium were discovered by Dr. Wollaston in 1803. These, like the two last-described metals, exist in the ore of platinum, from which rhodium may be obtained by the following process:—Digest crude platinum in a small quantity of nitro-muriatic acid, filter the saturated solution, and pour it into a solution of sal ammoniac, by which the greater proportion of the platinum is precipitated. Decant the clear liquor, and immerse a plate of zinc, which becomes coated with a black powder. Separate this, and digest it in dilute nitric acid, by which a little copper and lead are taken up. Then wash and digest in dilute nitro-muriatic acid, to which add some common salt, evaporate to dryness, and wash the dry mass repeatedly with alcohol. A deep red substance remains, which, when dissolved in water, furnishes a black precipitate upon the immersion of a plate of zinc. This, strongly heated with borax, assumes a white metallic lustre, and is rhodium.

Rhodium is very difficult of fusion; its specific gravity is

10.6. When pure, the acids do not dissolve it, but they act upon and dissolve several of its alloys, a circumstance which explains its presence in the nitro-muriatic solution of platinum. When an alloy of lead and rhodium is digested in nitro-muriatic acid, it is also readily dissolved, and by evaporation a red compound is obtained, from which muriate of rhodium may be separated by water. The rose-colour of this compound suggested the name which has been applied to the metal.

Solutions of rhodium are not affected by ferrocyanate of potassa, muriate of ammonia, hydrosulphuret of ammonia, nor carbonated alkalis. Pure alkalis throw down a yellow oxide, soluble in the acids and in excess of alkali; ammonia also occasions a yellow precipitate, very sparingly soluble in excess of that alkali.

Oxides of Rhodium.—Berzelius says there are three oxides of this metal: the *protoxide*, obtained by heating finely divided rhodium exposed to air to dull redness; at a higher temperature it is reduced; it is a black powder insoluble in the acids; the *deutoxide*, obtained by heating finely divided rhodium with potassa in an open silver crucible: the result, washed with water, furnishes a brown powder, which is a compound of the oxide and potassa, and may be decomposed by dilute nitric acid: the brown deutoxide remains undissolved; it combines with potassa and other salifiable bases, but does not form definite salts with the acids; the *peroxide* is precipitated by the caustic alkalis in the form of hydrate, from the solution of the triple muriate. The statement of the composition of these oxides, as given by Berzelius, is much at variance with that of Dr. Thomson. (*First Lines*, i. 460.) According to the latter, the equivalent of rhodium is 44, and the protoxide consists of one proportional of metal and one of oxygen, or $44 + 8 = 52$: the deutoxide of one of metal and one and a half of oxygen, or $44 + 12 = 56$; and the peroxide of one of metal and two of oxygen, or $44 + 16 = 60$. But further experiments are requisite to establish these numbers.

Sulphuret of Rhodium is obtained by heating the metal in a state of fine division with sulphur; or by heating the triple muriate of ammonia and rhodium with sulphur: it is also precipitated by heating the solution of the latter salt with one of

an alkaline hydrosulphuret. By the action of nitric acid it is converted into *sulphate of rhodium*.

Rhodium forms malleable *alloys* with the malleable metals, several of which have been examined by Dr. Wollaston.—*Phil. Trans.*, 1804. It has not been combined with mercury.

With steel, rhodium forms an alloy, which probably would be very useful in the arts, were it not for the scarcity of the latter metal. 1 to 2 *per cent.* of rhodium gives steel great hardness, and yet there is sufficient tenacity to prevent cracking either in forging or hammering.—*Quarterly Journal*, ix. 328.

The extreme hardness and durability of rhodium induced Dr. Wollaston to suggest it for the nibs of metallic pens, a purpose to which it has been successfully applied.

Section XXXV. PALLADIUM.

PALLADIUM is most easily obtained by the following process. (Wollaston, *Phil. Trans.* 1805.) Digest the ore of platinum in nitro-muriatic acid, neutralize the redundant acid by soda, throw down the platinum by muriate of ammonia, and filter. To the filtered liquor add a solution of cyanuret of mercury; a yellow flocculent precipitate of cyanuret of palladium is soon deposited, which yields palladium on exposure to heat.

The alcoholic *solution*, mentioned in the first paragraph of the preceding Section, contains the soda-muriates of palladium and platinum, from which the former metal may also be separated by cyanuret of mercury.

To obtain malleable palladium, Dr. Wollaston gives the following more explicit directions in his paper, printed in the *Phil. Trans.* for 1819:—

“ The residuum obtained from burning the precipitate of that metal is to be combined with sulphur, and each cake of the sulphuret, after being fused, is to be finally purified by cupellation, in an open crucible, with borax and a little nitre.

The sulphuret is then to be roasted, at a low red heat, on a flat brick, and pressed, when reduced to a pasty consistence, into a square or oblong and perfectly flat cake. It is again to be roasted very patiently, at a low red heat, until it becomes spongy on the surface. During this process, sulphur flies off in the state of sulphurous acid, especially at those moments when the heat is allowed occasionally to subside. The ingot is then to be cooled; and when quite cold, is to be tapped with a light hammer, in order to condense and beat down the spongy excrescences on its surface. The alternate roastings and tappings (or gentle hammerings) require the utmost patience and perseverance, before the cake can be brought to bear hard blows; but it may, by these means, at length be made so flat and square, as to bear being passed through the flattening-mill, and so laminated to any required degree of thinness.

“ Thus prepared, it is always brittle while hot, possibly from its still containing a small remnant of sulphur. I have also fused some palladium *per se*, without using sulphur; but I have always found it, when treated in this way, so hard and difficult to manage, that I greatly prefer the former process.”

Palladium is of a dull white colour, malleable and ductile. Its specific gravity is about 11.3. It is hard. It fuses at a temperature above that required for the fusion of gold, and when intensely heated by the oxy-hydrogen blowpipe, it is dissipated in sparks. When heated over the flame of a spirit lamp, it acquires various shades of blue upon its surface.

Dr. Wollaston has ascertained the existence of *native palladium* in the ore of platinum. It is in small fibrous grains.

Oxide of Palladium.—By carefully heating the nitrate of palladium to dull redness, a black oxide is obtained, which dissolves in muriatic acid, without evolving chlorine. When nitrate of palladium is precipitated by a caustic alkali, the red or dark orange coloured powder which falls is an *hydrated oxide*.

Chloride of Palladium.—When the nitro-muriate of palladium is evaporated to dryness, the residue may be heated till it fuses. At a high red heat it gives out chlorine, and is reduced.

Muriatic acid boiled upon palladium acquires a fine red

colour. Sulphuric acid becomes blue. Nitric acid readily dissolves it ; but its best solvent is the nitro-muriatic, which forms a fine red solution. The fixed alkalis throw down red or orange-coloured precipitates from these solutions, sparingly soluble in excess of the alkali. Ammonia precipitates a red triple salt. Ferrocyanate of potassa gives an olive-green precipitate; and sulphuretted hydrogen, one of a dark brown colour. Sulphate, nitrate, and muriate of potassa, produce an orange precipitate with the salts of palladium, as with those of platinum. Protomuriate of tin occasions a characteristic brown precipitate in the neutralized solutions of palladium ; and protosulphate of iron throws down metallic palladium.

Palladium and sulphur readily combine, and produce a white brittle compound, composed, according to Berzelius, of

Palladium	78.03
Sulphur	21.97
					<hr/>
					100

According to the same authority, oxide of palladium consists of

Palladium	87.56
Oxygen	12.44
					<hr/>
					100

From these analyses the number 56 may be assumed as the equivalent of palladium ; $56 + 8 = 64$ as that of the oxide ; and $56 + 16 = 72$ as that of the sulphuret.

The alloys of palladium have not been minutely examined. Like platinum, it destroys the colour of gold ; one part fused with six of gold forming a white alloy. This compound, from its hardness and durability, was employed, at the suggestion of Dr. Wollaston, for the graduated part of the mural circle, constructed by Mr. Troughton, for the Royal Observatory at Greenwich. It readily amalgamates with mercury.

It is probable that palladium exists in large quantities in some part of South America, for I have seen bars of it weighing several pounds imported from that country, and nearly pure.

Section XXXVI. SILICIUM.

FROM experiments upon the action of potassium upon silica, Sir H. Davy concluded that that earth consisted of a peculiar inflammable basis, combined with its weight of oxygen, and he called the basis *Silicium*. If, therefore, silica be considered as a protoxide, the number 8 will be the equivalent of silicium, and silica will consist of

1 proportional of silicium	=	8
1 ,, oxygen	=	8
					<hr/>	
Equivalent of silicium	=	16

This estimate of the composition of silica was deduced from the quantity of potassium required for its decomposition; the subject has since received further elucidation, and the correctness of the above statement has, to a great extent, been confirmed.

In the year 1824, silicium was obtained in its pure state by Berzelius, and from its properties, presently to be described, he has placed it, correctly perhaps, among the simple non-metallic combustibles; indeed, it bears a strong resemblance to boron. Before, however, we remove it from the class of bodies with which it has usually been associated, it may be well to wait till its general characters have been more satisfactorily studied. From the ample account of this body, given by Berzelius in his valuable "*Lehrbuch* *," the following details are chiefly extracted.

He recommends, as the best source of silicium, the silico-fluoride of potassium, which is prepared by passing silico-fluoric acid into a solution of potassa, evaporating to dryness, and heating the residue nearly, but not quite, to redness. The salt thus obtained is to be well mixed with eight or nine-tenths its weight of potassium, and the mixture introduced into a green glass tube and heated: before it acquires a red heat, its contents become ignited, in consequence of the chemical action

* Wöhler's German Translation, from the original Swedish, Dresden, 1825.

that ensues, and the potassium is burned at the expense of the silica ; a brown mass is thus obtained, consisting of fluoride of potassium, siliciuret of potassium, and a portion of undecomposed salt : this is thrown into cold water, which occasions the evolution of hydrogen, resulting from the action of the siliciuret, the potassium of which is converted into potassa, and the silicium set free. When the effervescence is over, and the fluid has become clear, it is poured off from the residue, which is again washed, allowed to subside, and separated by decantation as before. These first washings must be performed with cold water, otherwise the alkali re-acts on the silicium, which, however, may now be thoroughly edulcorated with boiling water. It remains in the form of a dark-brown powder, infusible, and a non-conductor of electricity. Its properties are remarkably different before and after the application of a red heat : *before it has been heated* it burns easily in the air ; but the superficial formation of silica prevents its entire combustion : in oxygen it burns brilliantly, and however carefully prepared, it always produces a little moisture. It is not acted upon either by sulphuric, nitric, or nitromuriatic acids, even when aided by heat. Liquid hydrofluoric acid readily dissolves it, evolving hydrogen : it is also dissolved when heated in a solution of caustic potassa. Silicium, *after it has been heated* *, sinks in sulphuric acid, is incombustible before the blowpipe and in oxygen, and is not acted on by hydrofluoric acid, nor by caustic potassa ; but it is easily dissolved in a mixture of hydrofluoric and nitric acids :

Silicium may be perfectly oxidized, and entirely converted into silica or *silicic acid* by mixing it with dry carbonate of potassa, and heating to redness ; it burns at the expense of the oxygen of the carbonic acid, and a silicate of potassa is obtained. Fused nitrate of potassa has no action upon it ; but the addition of a little dry carbonate of potassa causes immediate deflagration : this paradoxical appearance depends upon the circumstance that the attraction of silicium for oxygen is influenced by the presence of the alkali, which has a high attraction for silica ; just as the effect of zinc upon water is influenced by the presence of an acid, having an attraction for

* Obtained, for instance, by washing that which has been partially burned in the air with hydrofluoric acid, to remove the superficial silica.

the oxide of zinc about to be produced. Carbonic acid is so weak that it does not prevent the action of the alkali; and, as silicium has a much stronger attraction for oxygen than carbon, it is oxidized at the expense of the carbonic acid. Nitric acid, on the other hand, is a strong acid, which entirely prevents this action of the alkali in the saltpetre upon the silicium, and silicium, at the temperature at which saltpetre fuses, does not become oxidized; but if the heat be raised to whiteness, the silicium is then speedily oxidized by the decomposition of the nitric acid, and intense combustion ensues. Heated with the caustic alkalis, silicium burns in the oxygen of the water which they contain.

Oxide of Silicium, Silica, or Silicic Acid, is a very abundant natural product. It exists pure in some varieties of rock-crystal, and nearly pure in flint. It may be obtained by heating colourless rock-crystal to redness, quenching it in water, and reducing it to a fine powder; in this state it is silica almost perfectly pure. "Fuse one part of this powder with three of potassa in a silver crucible. Dissolve the mass formed, in water, add slight excess of muriatic acid, and evaporate to dryness. Wash the dry mass in boiling distilled water upon a filter, and the white substance which remains is silica." This is the usual process, but the earth obtained by simply reducing the colourless rock crystal to powder, is more pure; it only contains a trace of oxide of iron and manganese and of alumina. I have never been able to separate the last portions of alkali from silica precipitated from potassa.

Mr. Faraday informs me that a very pure silica may be obtained, by the fusion of fine white sand or powdered rock-crystal with carbonate of lime: the resulting compound of lime and silica may be decomposed by dilute muriatic acid, and the earth, after having been duly washed, is in the form of a very light powder. When silico-fluoric gas is passed into water, the silica which is precipitated, after having been washed and dried, is also extremely pure.

Silica, in its ordinary state, is a harsh white powder, insoluble in water and in most other solvents, and infusible except in the intense heat of the flame of a spirit-lamp, urged by the oxygen blowpipe: it then melts with difficulty into a colourless globule. Its specific gravity is 2.66.

When recently precipitated, and in the state of *hydrate*, it is to a certain extent soluble in water and in the acids. The aqueous solution is tasteless, and, when evaporated, deposits gelatinous silica, which, on being dried, becomes again quite insoluble: the acid solutions also exhibit no indication of saline combination, but when evaporated leave pure silica. Silica is often found in spring and mineral water; and in the fountains of Reikum and the boiling Geysers of Iceland it is contained in such quantities as to be deposited by them in the form of a porous incrustation.

Gelatinous silica dissolves in the fixed alkaline solutions; or when fused with thrice its weight of potassa, it forms a compound soluble in water (*liquor silicum*). This solution, after having been kept for a number of years, has occasionally deposited small crystals of silica. (In one case, crystals of sulphate of potassa were mistaken for those of silica.) I have seen in it a deposit very like chalcedony, and nearly as hard. Fused with a small quantity of alkali, silica forms *Glass*, the nature of which will presently be more particularly described.

Chloride of Silicium.—Silicium burns when heated in chlorine, or when a current of chlorine is passed over red-hot silicium in a porcelain tube, and a fuming liquid is the result, of a yellow colour, extremely volatile, and irritating to the nose and eyes, and which, exposed to moist air, forms muriatic acid and silica. Dropped into water it floats upon that fluid, and is then dissolved, depositing a little gelatinous silica: muriatic acid is also formed. When potassium is heated in its vapour, it burns with the production of siliciuret and chloride of potassium. It consists of

1	proportional of silicium	=	8
1	„	chlorine	.	.	.	=	36
							<hr/>
							44

Silicium has not been combined with iodine or bromine.

Fluoride of Silicium.—The only acid body which acts energetically upon silica is the hydrofluoric acid. The result of this action is a gaseous compound, which has been called *silicated fluoric acid*, or *fluo-silicic acid*; it is probably a binary compound of silicium and fluorine.

To obtain this gaseous compound, three parts of fluor spar

and two of powdered glass or of silica finely powdered, are mixed in a retort with about an equal weight of sulphuric acid; the gas evolved is to be collected over mercury, and when its production slackens, it may be accelerated by a gentle heat. The mercury and the glass vessels employed must be quite dry.

Silicated fluoric acid is a colourless gas; its odour is acrid, much resembling muriatic acid; its taste very sour; its specific gravity 3.61 compared with air: 100 cubic inches weigh 110.138 grains. It extinguishes the flame of a taper. It produces white fumes when in contact with damp air; and when exposed to water it is absorbed, and a soluble compound of silica with fluoric acid is formed; whilst a quantity of silica is at the same time precipitated. If the beak of the retort from which the gas is issuing be plunged into a basin of water, it is soon choked by the copious deposit of hydrated silica, which sometimes forms tubes through the water, by which the gas escapes directly into the air. When it is intended to saturate water with the gas (it takes up about 260 volumes), this effect may be prevented by agitation, or better by suffering the gas to escape through a stratum of mercury into water above it.

Water thus saturated becomes a gelatinous mass, from which the acid liquor may be separated, by placing it, without pressure, upon a linen filter. The liquor is sour, and, when saturated with the fixed alkalis, becomes gelatinous, but not turbid: with barytic salts it soon deposits a white precipitate. Saturated with potassa, and evaporated to dryness, it yields the *silico-fluoride of potassium*, already adverted to as a source of silicium. It is a hydrated silico-fluoric acid, and when evaporated, gaseous fluoride of silicium escapes, and hydrofluoric acid is evolved, so that, although the original aqueous solution does not act upon glass, it immediately does so when so far concentrated by evaporation as to generate the free hydrofluoric acid. According to Berzelius, fluoride of silicium is a compound of 71.68 fluorine, and 29.32 silicium.

When one volume of silicated fluoric acid is mixed with two of ammonia, a total condensation ensues, and a dry *silico-fluate of ammonia* results, which is decomposed by the action of water. When silico-fluoric gas is passed into liquid ammonia,

the whole of the silicium is separated in the form of a silica, and hydrofluat of ammonia remains in solution.

Potassium, when heated in this gas, burns and produces a silico-fluoride of potassium.

Sulphuret of Silicium.—When silicium is intensely heated in the vapour of sulphur, it burns into a white compound, which is little acted on by dry air; it immediately decomposes water, sulphuretted hydrogen is evolved, no sulphur is deposited, and the generated silica remains dissolved in the water. This, therefore, is a compound of

1	proportional of silicium	.	.	.	=	8
1	„ sulphur	.	.	.	=	16
					<hr/>	24

Glass is essentially a compound of silica with fixed alkali, a variety of other substances being occasionally added for particular purposes, among which oxide of lead is perhaps the most important. The silica used in the manufacture of glass is of various degrees of purity; fine white sand is generally employed in this country; flints, and the white quartz pebbles, abundant in some rivers, are also occasionally used. The alkali is either potassa or soda; purified pearlash being preferred for fine glass; while less pure substances, such as wood-ash, barilla, and kelp, are used for common glass, where the impurities contained in those alkalis are of no importance. The alkali is always in the state of carbonate, but it loses its carbonic acid during combination with the silica; the quantity employed is about half the weight of the silica, but there is some loss during the process, by evaporation*.

* All common glass when reduced to a fine powder is more or less acted on by boiling water, which separates the alkali, and its entire disintegration seems only to be prevented by the insolubility of the silica. Indeed, if finely powdered flint glass be placed upon turmeric paper and merely moistened, it powerfully reddens the test. Glass which has long been exposed to the weather frequently exhibits a beautiful iridescent appearance, and is so far decayed that it may be scratched with the nail: several years ago I examined some bottles of wine which had lain in a wet cellar near the Bank, upwards of 150 years, having been deposited there (as circumstances proved) previous to the great fire of London in 1666. The glass was soft and greatly corroded upon the surface, in consequence of the abstraction of its alkali. The wine appeared to have been Malaga and claret: the latter had perished, but the former was still vinous. See *Quarterly Journal*, xx. 262, where there is a paper on the solubility of glass, by Mr. T. Griffiths.

A glass composed solely of silica and alkali requires a very high temperature for its perfect fusion, and is very difficult to work, so that various substances are added, with the intention of forming a more fusible, colourless, dense, and transparent compound: oxide of lead, in the form of litharge or minium, is very efficacious in this respect; it increases the fusibility of the compound, gives it greater tenaciousness when red hot, increases its refractive power, and enables it to bear sudden changes of temperature. It is a copious ingredient in the *London flint glass*, celebrated for its brilliancy when cut, and used for most optical purposes. But lead, though it confers these advantages, is productive of some evil; it renders the glass so soft as easily to scratch, and so fusible that it softens at a dull red heat, a quality which, though sometimes desirable, is often disadvantageous in its chemical applications. It is also very difficult to obtain a mass of glass containing lead, of equal density throughout; it is generally wavy, a defect especially felt in selecting the object-glasses of telescopes.

Boracic acid and borax form an admirable flux for glass-making, but the expense of those materials confines them almost entirely to the manufacture of artificial gems, or of glass applicable to particular purposes only.

Black oxide of manganese has long been used in glass-making; it was formerly called *glass soap*, a term implying its power of cleansing certain impurities, and especially the green tinge which is apt to arise from impure alkali; but if it be added at all in excess, it communicates a purple tinge, more or less intense according to its quantity. This purple hue is destroyed by charcoal, or by thrusting a billet of wood into the glass-pot, which causes a slight effervescence, and the colour disappears. There can be little doubt that the carbon acts by deoxidizing the manganese, for if a little nitre be added, the purple colour returns. Lime in very small quantities (8 or 10 parts of chalk to 100 of silica) is sometimes added to glass; it acts as a flux, but it endangers the transparency of the compound.

White arsenic is also used as a very cheap and powerful flux; and nitre, in small quantities, is employed to destroy any impurities arising from carbonaceous matter.

The materials for the manufacture of glass are sometimes

submitted to an operation called *fritting*, before they are transferred to the regular glass-furnace. It consists in exposing them to a dull red heat, by which moisture and carbonic acid are expelled, and a slight degree of chemical action induced ; this also prevents the excessive swelling up of the materials in the glass-pots, and renders the process of vitrification more certain and expeditious. The term *frit*, however, is now generally applied to the mere mixture of materials, which, without previous preparation, are at once melted in the furnace.

The glass-pots are placed round a dome-shaped furnace, built upon arches, and open beneath for the free admission of air ; there are generally six in each furnace, and they are entirely enclosed except at an orifice on the side, opening into a small recess formed by the alternate projections of the masonry and the flues, in which recess the workmen stand. Coal is the fuel employed, and the furnace is so built that a rapid current of flame may be directed round each glass-pot, which afterwards passes out with the smoke into the dome and chimney, heating a broad covered shelf in its passage, which is the annealing oven.

In the construction of the furnace and pots the greatest care is required ; especially in the latter, which have not only to resist long-continued heat, but also, as far as possible, the action of ingredients which tend to accelerate their fusion or vitrification. They are usually made entirely of a refractory clay, one portion being crude or unburnt, and another calcined and powdered ; the latter being the remains of former furnaces when pulled down for repairs.

The frit is introduced into the glass-pots through the side-opening above mentioned, and being heated to bright redness, becomes of a pasty consistency, and at length perfectly fuses. A quantity of impurities subside to the bottom of the pot, and partly rise to its surface. The scum, known under the name of *sandiver* *, consists chiefly of saline substances, partly volatile at the high temperature of the furnace, which are removed from time to time, and sold to metal refiners as a powerful flux. The sandiver, or *glass gall*, being separated, the mate-

* This substance is scarcely known in our present glass-houses, in consequence of the pains bestowed upon the purification of the materials employed.

rials gradually become clearer, abundance of air-bubbles are extricated, and at length the glass appears uniform and complete; the fire round the individual pot is then damped till its contents acquire a consistency fit for working, the whole process requiring about 48 hours from the time the pots are filled. At the working heat, which is a full red, the glass has a very peculiar tenacious consistency, and as it adheres but feebly to polished metal, it is easily wrought and managed with iron tools.

All glass articles require to be carefully *annealed*, that is, suffered to cool very slowly, otherwise they are remarkably brittle and apt to crack, and even fly into many pieces upon the slightest touch of any hard substance, as is well shown in the small drops of green glass suddenly cooled by dropping them into water, and called *Rupert's drops*; the instant their thin end is broken off, they crumble into a powder with a kind of explosion. This phenomenon, according to Mr. Aikin, "depends upon some permanent and strong inequality of pressure, for when they are heated so red as to be soft, and merely let cool of themselves, the property of bursting is lost, and the specific gravity of the drop increased." What are termed *Proofs* or *Bologna phials* are also made of unannealed glass, and fly to pieces when a piece of flint or other hard and angular substance is dropped into them.

When large masses of glass which have been long in fusion are suffered to cool slowly, they frequently exhibit very singular crystalline appearances; there are often detached globular formations, of a very peculiar radiated texture, and looking exactly like foreign substances imbedded in the glass; sometimes it is opaque and crystalline, bearing a strong resemblance to certain mineral products: in these cases, crystallization seems to have influenced the affinity of the elements, and the consequent composition of the products. Mr. Watt's experiments upon the fusion of basalt may be consulted in reference to this curious subject. (*Phil. Trans.*)

The exact composition of the different kinds of glass is scarcely known*; the following proportions of the materials

* Mr. Faraday has lately communicated to the Royal Society a paper on the manufacture of glass for optical purposes, containing much curious and valuable information upon the subject generally: he has very successfully availed himself

are, however, given in Messrs. Aikin's *Dictionary*, to which the reader is referred for a valuable article upon the subject of glass: it must, however, be recollected, that the composition of the perfect glass can only be remotely anticipated from a knowledge of the substances employed in its formation, in consequence of the changes which they undergo, and the volatility of some of them, at the high temperature to which they are subjected.

Flint Glass.—Specific gravity about 3.2.

120	parts of	fine clear white sand
40	„	purified pearlash
35	„	litharge
13	„	nitre
A small quantity of black oxide of manganese.		

Crown Glass, or best window glass.

200	parts of	soda
300	„	fine sand
33	„	lime
250	„	ground fragments of glass *.

Green Bottle Glass.

100	parts of	sand
30	„	coarse kelp
160	„	lixivated earth of wood-ashes
30	„	fresh wood-ash
80	„	brick clay
100	„	fragments of glass.

Plate Glass, invented by Abraham Thevart in 1688, was first manufactured in Paris. It may be composed of

of the use of borate of lead as one of its components. I am indebted to him for the following comparative analyses of different specimens of flint-glass.

Silica	.	.	51.93	48.24	44.30
Oxide of lead	.	.	33.28	40.12	43.05
Potassa	.	.	13.77	10.60	11.75
Alumina	.	.	0.47	0.58	0.50
Oxides of iron and manganese	0.27		0.03	0.03	0.12
			<hr/> 99.72	<hr/> 99.62	<hr/> 99.72

* In the manufacture of all common glass a proportion of broken glass is usually mixed up with the raw materials, and is technically known under the name of *Cullet*.

300 lbs. fine sand
 200 lbs. soda
 30 lbs. lime
 32 oz. manganese
 3 oz. cobalt azure
 300 lbs. fragments of good glass.

These materials are brought into perfect fusion, and poured upon a hot copper-plate; the mass is then rolled out, annealed, and afterwards polished by grinding with sand, emery, and colcothar. The difficulty of producing a perfect plate without specks, bubbles, or waves, may easily be conceived, and this, with the risk of breakage, renders a large plate extremely expensive.

The art of *colouring glass*, and of making *artificial gems*, is of an old date, and effected by metallic oxides. The *paste* for artificial gems generally contains borax, and should be kept in fusion till perfectly clear. The following proportions are recommended by M. Douault-Wieland.—*Ann. de Chim. et Phys.*, tom. xix. 57.

	Grains.
Powdered rock-crystal	4056
Red lead	6300
Pure potassa	2154
Borax	276
Arsenic	12

M. Lançon gives the following as ingredients for a good paste:—

	Grains.
Litharge	100
White sand	75
White tartar or pot-ash	10

The metals employed as colouring materials are: 1. Gold. The purple of Cassius imparts a fine ruby tint. 2. Silver. Oxide or phosphate of silver gives a yellow colour. 3. Iron. The oxides of iron produce blue, green, yellow, and brown, depending upon the state of oxidizement and quantity. 4. Copper. The oxides of copper give a rich green; they also produce a red when mixed with a small proportion of tartar, which tends partially to reduce the oxide. 5. Antimony imparts a rich yellow. 6. Manganese. The black oxide of this metal, in large quantities, forms a black glass; in smaller quantities, various shades of purple. 7. Cobalt, in the state of oxide,

gives beautiful blues of various shades ; and with the yellow of antimony or lead it produces green. 8. Chrome produces fine greens and reds, depending upon its state of oxidizement.

The following are the best authorities upon the subject of coloured glasses and artificial gems :—Neri, *Art de la Verrerie*. Kunckel. Fontanien, *Encyclopédie Méthodique. Annales de Chim. et Phys.*, xiv. 57. Aikin's *Dictionary*, art. GLASS.

White Enamel is merely glass, rendered more or less milky or opaque by the addition of oxide of tin ; it forms the basis of many of the coloured enamels, which are tinged with the metallic oxides.

Directions for the preparation of several good enamel colours are given by Mr. Wynn, in the *Transactions of the Society of Arts*, 1817, and *Phil. Mag.* li.

It appears from the experiments of Mr. J. F. Daniell, that silicium exists in some of the varieties of cast iron (*Journal of Science and Arts*, vol. ii.) ; and an alloy containing it has been formed by MM. Stromeyer and Berzelius (Gilbert's *Annalen*, xxxviii.), by exposing a mixture of pure iron, silica, and charcoal, to an intense heat.

The fossils consisting of silica, pure, or nearly so, are principally the following :

Rock-crystal, or *Quartz*, which may be considered as pure silica. It crystallizes in the form of a six-sided prism, ended by six-sided pyramids ; some varieties are perfectly transparent and colourless ; others white and more or less opaque. Its specific gravity is 2.6. It is so hard as to give sparks when struck with steel, and is nearly infusible. The primitive crystal, which is very rare, is an obtuse rhomboid, the angles of which are $94^{\circ} 24'$, and $85^{\circ} 36'$. The finest specimens are brought from Madagascar and the Alps. The perfectly transparent crystals found near Bristol, and in Cornwall, are sometimes called *Bristol and Cornish diamonds*. The fine crystals are cut into ornaments, and sometimes used as a substitute for glass in spectacles ; they are then termed *pebbles*, and do not so readily become scratched as glass.

Brown and yellow crystals of Quartz are found in great beauty in the mountain of Cairn Gorm in Scotland, and are much admired for seal stones, &c. : they are sometimes improperly termed topazes.

Purple quartz or *amethyst*, is tinged with a little iron and manganese. *Rose quartz* derives its colour from manganese. *Prase*, or *green quartz*, contains actinolite; and *chrysoprase* is tinged of a delicate apple-green by oxide of nickel. *Avanturine* is a beautiful variety of quartz, of a rich brown colour, which, from a peculiarity of texture, appears filled with bright spangles; the finest specimens are from Spain: it is often imitated. Small crystals of quartz, tinged with iron, are found in Spain, and have been termed *Hyacinths of Compostella*.

ii. *Flint*, *Chalcedony*, *Carnelian*, *Onyx*, *Sardonyx*, and *Bloodstone* or *Heliotrope*, and the numerous varieties of *Agates*, are principally composed of quartz, with various tinging materials.

iii. *Opal* is among the most beautiful productions of the mineral world; it is a compound of about 90 silica and 10 water, and is distinguished by its very brilliant play of colours. The finest specimens come exclusively from Hungary. There is a variety of opal called *Hydrophane*, which is white and opaque till immersed in water; it then resembles the former.

Common opal is usually of a dirty white, and does not exhibit the colours of the noble opal; it contains silica and water, with a little oxide of iron, and is not of unfrequent occurrence. The substance called *menilite* from Menil Montant, near Paris, is nearly allied to common opal. It is found in irregular masses in a bed of clay.

iv. *Pitchstone*, so called from its resinous appearance, contains 73 *per cent.* of silica. *Obsidian*, a volcanic product, contains 78 *per cent.* of silica, and much resembles glass in appearance; and the different kinds of *pumice* are nearly of similar composition.

Section XXXVII. ALUMINUM.

THE earth alumina constitutes some of the hardest gems, such as the sapphire and ruby; and combined with water, it gives a peculiar softness and plasticity to some earthy compounds, such as the different kinds of clay. That this sub-

stance is a metallic oxide was first demonstrated by Davy, who found that potassa was generated by passing the vapour of potassium over white-hot alumina: he did not, however, determine the properties of its base. This has since been more accurately effected by Wöhler, to whom we owe the following ingenious method of obtaining it (*Ann. de Chim. et Phys. Jan. 1828*). Chloride of aluminum is heated with potassium in a small platinum crucible; the heat of a spirit lamp is sufficient, for when the substances begin to act, the temperature suddenly rises to redness, and care should be taken so to adjust the relative proportions of materials, that none of the chloride may be evaporated in an undecomposed state, while at the same time there should not be excess of alkali in the residue. When the crucible is cold its contents are well washed with cold water, by which a finely-divided gray substance with a certain degree of metallic lustre is obtained, which is pure aluminum. It is extremely difficult of fusion; and although in the pulverulent state it does not apparently conduct electricity, it becomes a conductor when its particles are aggregated by fusion. This is an interesting fact, and holds good also, according to Wöhler, in the case of iron, which does not conduct when in very fine powder. Aluminum is not oxidized by mere exposure to air, but when heated nearly to redness, it burns into a hard white substance, having the properties of alumina. When sprinkled into the flame of a spirit-lamp it scintillates like iron filings, and if, when red-hot, it be immersed in oxygen, it burns with vivid light and intense heat: the result is fused alumina, apparently as hard as corundum.

Aluminum is not acted on by water at common temperatures, but when boiled it is slightly oxidized, and a little hydrogen is evolved: the oxidizement is, however, imperfect and superficial. It is not affected by nitric or sulphuric acids at common temperatures, but it rapidly dissolves in hot sulphuric acid, and sulphurous acid is evolved. The dilute acid dissolves it with the evolution of hydrogen, as is also the case with muriatic acid. It is soluble with the evolution of hydrogen in caustic ammonia and potassa, and alkaline solutions of alumina are the results.

Oxide of Aluminum—Alumina.—To obtain pure alumina

we add carbonate of ammonia to a solution of alum, wash till the waters no longer affect a solution of muriate of baryta, and ignite the precipitate; or, it may be procured, according to Gay-Lussac (*Ann. de Chim. et Phys.* v. 102), in a state of great purity, by igniting ammonia-alum previously deprived of water of crystallization by heat: sulphate of ammonia evaporates, and alumina remains, perfectly white and very soft to the touch. It readily blends with water, but assumes its former properties after having been gently heated. Its extreme division, and the hardness of its particles, observes Gay-Lussac, might render it useful for polishing metal, and its whiteness for the preparation of colours.

Alumina is a colourless, insipid, insoluble powder, without action upon vegetable blues: its specific gravity is 2. It has a strong attraction for moisture, which it rapidly absorbs from humid air, to the amount of one-third its own weight. When precipitated from its solution, and dried at a temperature of 60°, it retains about half its weight of water; this may be expelled by ignition. When mixed with water, alumina is characterized by the plasticity of the mixture; and if the paste be dried in the air, and then heated, it shrinks considerably in consequence of the loss of water: this shrinkage was employed by Mr. Wedgwood as a measure of temperature (vol. i. p. 38). Alumina has a strong affinity for various organic compounds, and its use in the arts of dyeing and calico-printing depends upon its attraction for different colouring principles. Thus, if ammonia be added to a solution of alum in infusion of cochineal, or of madder, the aluminous earth falls in combination with the red colouring matter, and the supernatant liquor remains colourless. Colours thus prepared are called *Lakes*.

Moist alumina is readily soluble in most of the acids; but after the expulsion of its water by a red heat, it is much more difficultly dissolved. It is very sparingly soluble (when moist) in caustic ammonia; but potassa and soda readily dissolve it, and it is also soluble, to a certain extent, in the aqueous solutions of baryta and strontia. The fixed alkaline solutions are decomposed by the acids and by ammoniacal salts. Some of the earthy combinations of alumina exist native, and in them it has been regarded as performing the part of an acid; so that

they have been called *Aluminates*. Alumina is recognized by its solubility in caustic potassa; by the formation of octoëdral crystals of alum on evaporating its sulphuric solution with the addition of sulphate of potassa; and by the fine blue colour which it affords when moistened with nitrate of cobalt and strongly heated: this, according to Berzelius, is the most certain test.

Different authorities are too much at variance in respect to the composition of alumina, to enable us to determine its equivalent, or that of aluminum, with any satisfactory precision. Berzelius says that alumina consists of 53.3 aluminum, 46.7 oxygen; so that upon this datum, 9 and a fraction would be the equivalent for aluminum: Dr. Thomson assumes the number 10, which, as deduced from the analysis of some of its salts, may apparently be adopted without material error: but the whole inquiry upon this subject demands revision.

Chloride of Aluminum, already mentioned as a source of the metal, was obtained by Wöhler, as follows:—Alumina, in the state of pulverulent hydrate, is mixed into a paste with powdered charcoal, oil, and sugar, and this is heated in a covered crucible till the organic matter is destroyed: an intimate mixture of the earth with charcoal is thus obtained, which is introduced whilst hot into a proper porcelain or glass tube, placed in a convenient furnace; dried chlorine is then passed through it into a receiver attached to the other end of the tube, and the air being thus expelled, the tube is heated red hot, and chlorine gradually passed into it: carbonic oxide is disengaged, and chloride of aluminum formed, which chiefly collects within the tube, and ultimately plugs it up. It is a crystalline translucent substance of the colour of chlorine; it fumes and deliquesces when exposed to air, and is energetically acted upon by water, which yields a solution of muriate of alumina. It is probably a compound of one proportional of each of its constituents.

Chlorate of Alumina is a deliquescent salt.

Iodide and Bromide of Aluminum have not been examined.

Fluoride of Aluminum.—Hydrate of alumina readily dissolves in hydrofluoric acid, and, on evaporation, a gummy substance is obtained, which bears a red heat without entire

decomposition. It cannot be crystallized. Berzelius has described several triple salts, formed by dissolving the alkalis and alumina in hydrofluoric acid.

Nitrate of Alumina is very difficultly crystallizable, and generally obtained on evaporating its solution in the form of a semitransparent gum-like mass, very deliquescent and soluble in alcohol. When decomposed by caustic ammonia, a pasty precipitate separates, which is a *subnitrate*, not decomposed by excess of ammonia. (Berzelius.)

Sulphuret of Aluminum is obtained by dropping sulphur upon incandescent aluminum; a black compound is the result, which is decomposed by exposure to air, and which, when thrown into water, deposits alumina, and evolves sulphuretted hydrogen: it probably, therefore, contains one proportional of each of its components.

Sulphate of Alumina is formed by digesting hydrate of alumina in sulphuric acid, diluted with an equal bulk of water: the solution is evaporated and alcohol added, which throws down the sulphate. It dissolves in two parts of water, and forms small lamellar crystals, of a sweet and astringent taste. Exposed to heat, this salt loses water of crystallization to the extent of 46.6 *per cent.*, and an anhydrous sulphate remains, composed probably of 1 proportional of alumina = 18 + 1 of sulphuric acid = 40. By long exposure to a red heat, the whole of the acid is expelled. This salt may be used as a test for potassa; for when it is dropped into a strong solution of that alkali or its salts, alum is thrown down.

Common Alum.—This salt is usually prepared by roasting and lixiviating certain clays containing pyrites; to the leys, a proper quantity of sulphate of potassa is added, and the triple salt is obtained by crystallization.

Alum has a sweetish astringent taste. It dissolves in five parts of water at 60°, and the solution reddens blues. It furnishes very perfect octoëdral crystals. In its crystalline form it consists, according to Mr. R. Phillips, of

Sulphate of alumina	.	.	.	123.00
Bisulphate of potassa	.	.	.	119.32
Water	.	.	.	187.00
				<hr/>
				429.32

Mr. Phillips adopts the number 27 as the representative of alumina, and considers alum as a compound of 2 proportionals of sulphate of alumina, 1 of bisulphate of potassa, and 25 of water. These proportions, therefore, would be

Bisulphate of potassa	.	.	.	=	128
Sulphate of alumina (67 × 2)	.	.	.	=	134
Water (9 × 25)	.	.	.	=	225
					<hr/>
					487

Dr. Thomson arrives at the same equivalent for alum, by considering it as a compound of

1	proportional of sulphate of potassa	.	.	=	88
3	proportionals of sulphate of alumina (58 × 3)	.	.	=	174
25	„ water (9 × 25)	.	.	=	225
					<hr/>
					487

When alum is exposed to an intense heat, it loses water, and a portion of acid; but the whole of the acid cannot be expelled. It becomes light and spongy; and in this state is called in the *Pharmacopœia*, *Alumen ustum*, or *exsiccatum*. Alum sometimes forms cubic crystals, and is known under the name of *cubic alum*. Some varieties of alum contain ammonia.

When alum is ignited with charcoal, a spontaneously inflammable compound results, which has long been known under the name of *Homborg's pyrophorus*. The potassa appears to be decomposed in this process, along with the acid of the alum, and pyrophorus is probably a compound of sulphur, charcoal, and potassium, with alumina.

Pyrophorus is most successfully prepared by the following process. Mix equal parts of honey, or of brown sugar and powdered alum, in an iron ladle, melt the mixture over a fire, and keep it stirred till dry: reduce the dry mass to powder, and introduce it into a common phial coated with clay, and placed in a crucible of sand. Give the whole a red heat, and when a blue flame appears at the neck of the phial, allow it to burn about five minutes, then remove it from the fire; stop the phial, and allow it to cool, taking care that air cannot enter it. (See SULPHATE OF POTASSA.)

Alum is of extensive use in the arts, more especially in dyeing and calico-printing, in consequence of the attraction which alumina has for colouring matter.

Sulphate of Alumina and Ammonia, or *Ammoniacal Alum*, has been described by Riffault (*Ann. de Chim. et Phys.* ix. 106), composed of

1	proportional of sulphate of ammonia
3	proportionals of sulphate of alumina
24	„ water.

A *Subsulphate of Alumina and Potassa*, and a *Subsulphate of Alumina and Ammonia* are also described by M. Riffault. (*Ann. de Chim.* xvi. 355.)

A *sulphate of alumina and soda*, or *soda alum*, is described in the *Quarterly Journal of Science and Arts* (viii. 386), in the form of irregular efflorescent octoëdra: it appears to contain

2	proportionals of sulphate of alumina
1	proportional bisulphate of soda
28	proportionals of water.

Phosphuret of Aluminum is formed by passing the vapour of phosphorus over red-hot aluminum. Exposed to air it smells of phosphuretted hydrogen, and it decomposes water.

Phosphate of Alumina is insoluble in water, but it dissolves in phosphoric acid, and yields on evaporation a gummy deliquescent compound. When excess of ammonia is added to an acid solution of the phosphate, a *subphosphate of alumina* is precipitated, which is soluble in caustic potassa. The mineral called *Wavellite* is a hydrated subphosphate of alumina.

Seleniuret of Aluminum is a black pulverulent compound rapidly decomposed by water.

Borate of Alumina may be formed by boiling recently precipitated alumina with boracic acid: it is uncrystallizable, and of a very astringent taste.

A native *sulphate of alumina and iron* in silky fibres, was analyzed by Mr. Phillips (*Ann. of Phil.* v.), and was found composed of

Sulphuric acid	.	.	.	30.9	or 4 atoms	160
Protoxide of iron	.	.	.	20.7	„ 3 „	108
Alumina	.	.	.	5.2	„ 1 „	27
Water	.	.	.	43.2	„ 25 „	225
				<hr/>		<hr/>
				100.		520

Alloys of Aluminum.—There can be little doubt of the exist-

ence of aluminum, as well as of silicium and calcium, and probably magnesium, in some of the varieties of cast-iron and steel. By fusing highly carburetted steel with alumina, a peculiar alloy results, which is white, granular, and brittle, and which yields on analysis 6.4 *per cent.* alumina. On fusing 67 parts of this alloy with 500 of steel, a compound is obtained, which possesses all the characters of the best Bombay wootz, and like it, when its surface is polished and washed over with dilute sulphuric acid, exhibits the striated appearance called *damask*, for which the celebrated sabres of Damascus are remarkable, and which renders it probable that they also are made of wootz. (*Quarterly Journal of Science and Arts*, ix.) Many of the varieties of cast-iron afford lime and silica when dissolved in acids, and it is highly probable that those substances, as well as the alumina in the wootz, exist combined with the iron in their deoxidized or metallic state.

Aluminous Minerals.—Under the term *corundum* certain mineral substances have been included, composed of alumina, nearly pure.

Perfect corundum occurs crystallized in six-sided prisms, transparent and colourless. Its specific gravity is about 4. When blue, it constitutes the *sapphire*; when red, the *ruby*; when yellow, the *oriental topaz*, or *chrysolite*. These gems are principally found in alluvial deposits. They are mostly procured from Ceylon and Pegu; they have also been found in France and in Bohemia. *Imperfect corundum*, or *adamantine spar* and *emery*, are nearly analogous in composition to the former; they contain from 3 to 5 *per cent.* of silica and 1 to 2 of oxide of iron. *Spinelle*, or *balass ruby*, is found in octoëdral crystals, of a red colour. It is composed of 74.5 alumina, 15.5 silica, 3.25 magnesia, 1.5 oxide of iron, and traces of lime and oxide of chrome. The *ceylanite*, or *pleonaste*, is a variety of spinelle. A variety, containing oxide of zinc, is called *zinc spinelle*, or *automalite*. The mineral, called *Wavellite*, or *hydrargillite*, is a compound of alumina, phosphoric acid, and water. It is found in Devonshire, in small radiated nodules upon clay-slate. According to Berzelius (*Ann. de Chim. et Phys.*, tom. xii.), 100 parts afford

Alumina	35.35
Phosphoric acid	33.40
Fluoric acid	2.06
Lime	0.50
Oxides of iron and manganese	1.25
Water	26.80
						<hr/> 99.36

The *occidental topaz*, found chiefly in Saxony, Siberia, Brazil, and Scotland, consists of alumina, silica, and fluoric acid. The *schorlous beryl* or *pycnite*, and the *pyrophysalite*, are nearly of the same composition. *Cryolite*, a rare substance hitherto only found in Greenland, consists of alumina, soda, and fluoric acid. It is white, amorphous, and translucent. A mineral, called *native alumina*, is found upon the Sussex coast, near Newhaven. It is white and friable, and occurs massive and encrusting. It contains alumina, sulphate of lime, and sulphate of alumina.

A very numerous and important class of minerals consists of a combination of silica with alumina, in various proportions, and with the occasional addition of the fixed alkalis or alkaline earths, and a few of the other metallic oxides: the principal of these, which are not elsewhere mentioned, are the following:—

Zeolite.—Of this mineral there are several varieties. The principal are the *radiated* or *mesotype*; the *nacreous* or *stilbite*; the *efflorescent* or *laumonite*; and the *cubic* or *analcime*. These minerals fuse and intumesce before the blowpipe, and mostly form gelatinous solutions in the acids. The following is Vauquelin's analysis of a radiated or acicular zeolite:—

Silica	50.24
Alumina	29.30
Lime	9.46
Water	10.00

Apophyllite and *Chabasite* are nearly of the same composition; except that the latter contains about 9 per cent. of potassa and soda.

Garnet occurs massive, but generally crystallized in dodecaëdra. The *precious garnet* is red and transparent; the *common garnet*, red, brown, or green. According to Vauquelin, the precious garnet consists of

Silica	36
Alumina	20
Oxide of iron	41
Lime	3

The *cinnamon stone* of Ceylon is nearly of similar composition.

Melanite, or *black garnet*, contains, upon the same authority,

Silica	35
Alumina	6
Lime	32
Oxides of iron and manganese	25

Leucite, or *white volcanic garnet*, contains, according to Klaproth,

Silica	54
Alumina	24
Potassa	21

Vesuvian, or *idocrase*, is brown or yellow-red, and is found crystallized in the masses of rock ejected by Vesuvius and Etna. It has also been found in the Alps and in Siberia. The Neapolitan lapidaries call it *chrysolite of Vesuvius*. In composition it differs little from melanite.

Staurotide, or *grenatite*, crystallizes in four and six-sided prisms often crossing each other. It consists of

Silica	33
Alumina	44
Lime	3.8
Oxides of iron and manganese	14

Sodalite and *natrolite* are minerals containing a considerable portion of soda. The former has been analyzed by Dr. Thomson. It has hitherto only been found in Greenland and on Vesuvius. Its colour is light green, and it occurs massive and crystallized in rhomboidal dodecaëdra. It consists of

38.42 silica
27.48 alumina
23.50 soda
2.70 lime
3.00 muriatic acid
1.00 oxide of iron
2.10 volatile matter

Prehnite is of a greenish colour, and radiated fracture. It occurs massive and crystallized in prisms. A lamellar variety

has been called *koupholite*. It is found near the Cape of Good Hope, and in France and Scotland.

Spodumene, or *triphane*, is a mineral already alluded to in the section on Lithium. It is nearly allied to feldspar, and consists of

65	silica
25	alumina
8	lithia
2	oxide of iron

100

Scapolite, and *Elaolite*, or *Fettstein*, are minerals hitherto found only in Norway: they contain about 45 *per cent.* of silica, and 33 of alumina. The scapolite contains about 18 *per cent.* of lime; the *elaolite*, the same proportion of potassa and soda.

Nephritic stone, or *jade*, which is found in the Alps, and in China and India, contains, according to Saussure,

53.7	silica
12.7	lime
7	oxide of iron and manganese
10.7	soda
8.5	potassa
7.4	water and loss.

100.0

The Chinese cut this substance into figures, and it is sometimes used for the handles of cutting-instruments. In New Zealand and other islands of the Pacific Ocean it is used for cutting instruments, in consequence of its hardness and toughness. Hence it has been called *axe stone*.

Schorl and *Tourmalin* consist principally of silica, alumina, and oxide of iron. They occur in prismatic crystals of a black colour.

Thallite, *epidote*, or *pistacite*, is nearly allied in composition to schorl. It occurs in green prismatic crystals.

Axinite, or *thumerstone*, is found crystallized in flat oblique rhombs, of a brown, bluish, or gray tint, and transparent. It consists, according to Vauquelin, of

Silica	44
Alumina	18
Lime	19
Oxide of iron	14
Oxide of manganese	4

Cyanite is of a blue and gray colour, translucent, and occurs massive and prismatic. It consists, according to Klaproth, of

Alumina	55.5
Silica	43.0
Oxide of iron	0.5

Lepidolite occurs massive, and of a purplish colour and lamellar texture. According to Klaproth, it contains

Silica	54.5
Alumina	38.25
Potassa	4.
Oxide of iron and manganese	0.75

Actinolite is of a green colour, and generally occurs in aggregated masses of prismatic crystals. It contains

Silica	50.
Lime	9.7
Magnesia	19.2
Alumina	0.7
Oxides of chrome and iron	8.

Tremolite is nearly white, fibrous, and semi-transparent. It contains

Silica	62
Lime	14
Magnesia	13
Oxide of iron	6

Asbestos is a soft fibrous flexible mineral, of a white or greenish tint, composed of

Silica	60
Magnesia	30
Lime	6
Alumina	4

Amianthus, *mountain cork*, and *mountain wood*, are varieties of asbestos.

Lapis lazuli consists of

Silica	46
Carbonate of lime	28
Alumina	14
Sulphate of lime	6.5
Oxide of iron and water	5

The blue colour is probably derived from some principle which has hitherto escaped analysis. It is prepared for painters under the name of *ultra-marine*.

Harmotome, *Staurolite*, or *Cross-stone*, occurs in small quadrangular prisms terminated by four rhombic planes, crossing each other. It is also found in single crystals. It is found at Andreasberg, in the Hartz, and at Strontian, in Scotland. It consists, according to Klaproth, of

Silica	49
Alumina	16
Baryta	18
Water	15

Augite is a mineral of a black or brownish green colour, found in volcanic products, and in some basalts. *Sahlite* and *coccolite* are varieties of augite. It is composed of

Silica	52
Lime	13
Oxide of iron and manganese	16
Magnesia	10
Alumina	9

Datholite is a combination of

Silica	38
Lime	34
Boracic acid	22
Water	4

It has only been found in Norway.

Under the term *Clay* is comprehended a variety of mixtures of silica and alumina, more or less pure, and characterized by a peculiar plasticity in their moist state. The following are the principal varieties.

1. *Porcelain Clay*, derived principally from the decomposition of feldspar, and containing silica and alumina, sometimes with traces of oxide of iron; it is very difficult of fusion.
2. *Marly Clay*, which, with silica and alumina, contains a portion of carbonate of lime; it is much used in making pale bricks, and as a manure; and when highly heated enters into fusion.
3. *Pipe Clay*, which is very plastic and tenacious, and requires a higher temperature than the preceding for fusion; when burned it is of a cream colour, and used for tobacco-pipes and white pottery.
4. *Potters' Clay*, is of a reddish or gray colour, and becomes red when heated; it fuses at a bright red heat: mixed with sand it is manufactured into red bricks and tiles, and is also used for coarse pottery.

The better kind of *pottery*, called in this country *Staffordshire ware*, is made of an artificial mixture of alumina and silica; the former obtained in the form of a fine clay, from Devonshire chiefly; and the latter, consisting of chert or flint, which is heated red-hot, quenched in water, and then reduced to powder. Each material, carefully powdered and sifted, is diffused through water, mixed by measure, and brought to a due consistency by evaporation: it is then highly plastic, and formed upon the potter's wheel and lathe into various circular vessels, or moulded into other forms, which, after having been dried in a warm room, are enclosed in baked clay cases resembling bandboxes, and called *seggars*; these are ranged in the kiln so as nearly to fill it, leaving only space enough for the fuel; here the ware is kept red-hot for a considerable time, and thus brought to the state of *biscuit*. This is afterwards *glazed*, which is done "by dipping the biscuit ware into a tub containing a mixture of about 60 parts of litharge, 10 of clay, and 20 of ground flint, diffused in water to a creamy consistence, and when taken out, enough adheres to the piece to give an uniform glazing when again heated. The pieces are then again packed up in the seggars, with small bits of pottery interposed between each, and fixed in a kiln as before. The glazing mixture fuses at a very moderate heat, and gives an uniform glossy coating, which finishes the process when it is intended for common white ware."—Aikin's *Dictionary*. Art. POTTERY.

The patterns upon ordinary porcelain, which are chiefly in blue, in consequence of the facility of applying cobalt, are generally printed off upon paper, which is applied to the plate or other article while in the state of biscuit, and adheres permanently to the surface when heat is properly applied.

The manufacture of *porcelain* is a most refined branch of art; the materials are selected with the greatest caution, it being necessary that the compound should remain perfectly white after exposure to heat: it is also required that it should endure a very high temperature without fusing, and at the same time acquire a semivitreous texture and a peculiar degree of translucency and toughness. These qualities are united in some of the oriental porcelain, or *China*, and in some of the old Dresden, but they are rarely found co-existent in that of

modern European manufacture. Some of the French and English porcelain, especially that made at Sèvres and at Worcester, is extremely white and duly translucent, but it is more apt to crack by sudden changes of temperature; more brittle, and consequently requires to be formed into thicker and heavier vessels; and more fusible than the finest porcelains of Japan and China.

The colours employed in painting porcelain are the same metallic oxides enumerated for colouring glass, and in all the more delicate patterns they are laid on with a camel-hair pencil, and generally previously mixed with a little oil of turpentine. Where several colours are used, they often require various temperatures for their perfection; in which case those that bear the highest heat are first applied, and subsequently those which are brought out at lower temperatures. This art of painting on porcelain or in enamel is of the most delicate description; much experience and skill are required in it, and with every care there are frequent failures; hence it is attended with considerable expense. The gilding of porcelain is generally performed by applying finely-divided gold mixed up with gum-water and borax; upon the application of heat the gum burns off, and the borax vitrifying upon the surface causes the gold firmly to adhere; it is afterwards burnished.

In the manufacture of various kinds of pottery employed in the chemical laboratory, and especially in regard to *crucibles*, many difficulties occur; and many requisites are necessary, which cannot be united in the same vessel: to the late Mr. Wedgwood we are indebted for vast improvements in this as well as in other branches of the art.

Crucibles composed of one part of pure clay mixed with about three parts of coarse and pure sand, slowly dried and annealed, resist a very high temperature without fusion, and generally retain metallic substances; but where the metals are suffered to oxidize, there are few which do not act upon any earthen vessel, and some cause its rapid fusion, as the oxides of lead, bismuth, &c. Where saline fluxes are used, the best crucibles will always suffer, but platinum may often be employed in these cases, and the chemist is thus enabled to combat many difficulties which were nearly insurmountable before this metal was thus applied.

Whenever siliceous and aluminous earths are blended, as in the mixture of clay and sand, the compound softens, and the vessel loses its shape when exposed to a long-continued white heat, and this is the case with the *Hessian* crucibles: consequently, the most refractory of all vessels are those made entirely of clay, coarsely-powdered burned clay being used as a substitute for the sand. Such a compound resists the action of saline fluxes longer than any other, and is therefore used for the pots in glass furnaces. A Hessian crucible lined with purer clay is rendered much more retentive; and a thin china cup or other dense porcelain resists the action of saline matters in fusion for a considerable time.

Plumbago is a very good material for crucibles, and applicable to many purposes: when mixed with clay it forms a very difficultly fusible compound, and is protected from the action of the air at high temperatures; it is well calculated for small table furnaces. Wrought-iron and the best cast-iron crucibles are used for the fusion of several metallic substances which melt at a bright red heat.

Under the term *Lutes* a variety of compounds are used by the practical chemist for the purpose of securing the junctures of vessels or protecting them from the action of heat. Slips of wetted bladder, linseed meal made into a paste with gum-water, white of egg and quicklime, glaziers' putty, which consists of chalk and linseed oil, and *fat lute*, composed of pipe-clay and drying oil, well beaten to a stiff mass, are very useful lutes for retaining fumes and vapours and joining vessels to each other, but earthy compounds are required to withstand the action of a high temperature.

Windsor loam, or an artificial mixture of clay and sand well beaten into a stiff paste, and then thinned with water and applied by a brush in successive layers, to retorts, tubes, gun-barrels, &c., enables them to bear a very high temperature; if a thick coating is required, great care should be taken that the cracks are filled up as it dries, and often a little tow mixed up with the lute renders it more permanent and applicable. If the lute is intended to vitrify, as, for instance, to prevent the porosity of earthenware at high temperatures, a portion of borax or of red lead may be mixed up with it. Respecting the general selection and management of crucibles, lutes, &c., the reader is referred to Mr. Faraday's *Manipulation*.

Mortar, or the cement used in building, is a compound of several earthy substances, one of which is always lime: for much valuable information relating to this important subject we are indebted to the late Mr. Smeaton, (*History of the Eddystone Lighthouse*,) and an excellent summary of the principal facts connected with it will be found in Aikin's *Dictionary*—Art. CEMENTS. The ordinary mode of making mortar consists in mixing a quantity of common sand with slacked lime, without any careful attention to the quantity or purity of the materials; but it has been shown by Mr. Smeaton, that the presence of unburnt clay prevents the induration of the mortar, and the sand used in London always contains it; the lime too is often imperfectly burned and seldom duly selected; that which contains a portion of alumina and oxide of iron being preferable to the purer varieties: hence the advantage of *Dorking* lime, or *meagre lime*, as it is usually called. The sand should be sharp and large grained, and perfectly free from salt, which always prevents the mixture from becoming hard. The addition of calcined ferruginous clay, or calcined basalt, or black oxide of iron, gives mortar the property of becoming hard under water.

The mutual action which the substances constituting the different kinds of mortar undergo, has hitherto been but imperfectly examined by the chemist; to M. Vicat we are indebted for a curious and important series of investigations upon this subject, and his work may be consulted with much advantage, by those who are concerned in investigations of this nature.—*Recherches Expérimentales sur les Chaux de Construction, les Bétons, et les Mortiers ordinaires.* Paris, 1818.

Section XXXVIII. ZIRCONIUM.

SIR H. DAVY first demonstrated the nature of *Zirconia*, and its metallic base has since been obtained by Berzelius by a process analogous to that which he employed in decomposing silica. Zirconium is thus procured in the form of

a black powder, difficultly soluble in the acids, with the exception of the hydrofluoric, which readily dissolves it, evolving hydrogen. Heated in the atmosphere, it readily burns into zirconia.

The earth *zirconia*, or the *oxide of zirconium*, is a white insipid substance; specific gravity 4.3; it is found in the *zircon* or *jargon* of Ceylon. It is characterized by insolubility in pure alkalis, but is soluble in the fixed alkaline carbonates, and sparingly in carbonate of ammonia. It dissolves in most of the acids when recently precipitated, and its salts are distinguished from those of alumina and glucina, by furnishing precipitates to the caustic alkalis insoluble in excess of precipitant. Its muriatic solution becomes turbid, and gelatinizes on concentration. Oxalic acid throws down a white precipitate in it, as do also tartaric acid, tartrate of potassa, and malic acid. It is precipitated of a greenish blue colour by ferrocyanate of potassa, and dark olive by hydrosulphuret of ammonia. It has been remarked by Pfaff, that in many of their properties there is a resemblance between zirconia and oxide of titanium: but tincture of galls throws down yellow flakes in a solution of zirconia, whereas it precipitates titanium of a red-brown. (*Ann. of Phil.* xiii. 83.)

i. The *zircon*, or *jargon*, is a mineral, usually of a gray, yellowish, or reddish-brown colour, crystallized in octoëdrons and four-sided prisms, and generally semi-transparent.

ii. *Zirconia* is contained in the *hyacinth*, which is also found in Ceylon, and in various parts of Europe. Its usual colour is red or reddish, and its crystals small flattened octoëdra, or four-sided prisms. These minerals contain about 70 *per cent.* of zirconia each, the remainder being silica, with a trace of oxide of iron.—Klaproth's *Beitrag*e, vol. i. pp. 222 and 231.

Zirconia is obtained by the following process:—Reduce the stone to a fine powder, having previously heated it to redness, and quenched it in water. Mix the powder with nine times its weight of pure potassa, and gradually project it into a red-hot silver crucible, and keep it in perfect fusion for two hours. When the crucible has cooled, reduce the mass to a fine powder, and boil it in distilled water. Boil the undissolved residue in muriatic acid; filter, and evaporate to dryness; redissolve the dry mass in distilled water, and precipitate by

carbonate of soda. The carbonate of zirconia which falls may be decomposed by heat.

The following method of obtaining pure zirconia is recommended by MM. Dubois and Silveira. (*Annales de Chim. et Phys.*, xiv. 110.) Powder the zircons very fine, mix them with two parts of pure potassa, and heat them red-hot in a silver crucible for an hour. Treat the substance obtained with distilled water, pour it on a filter, and wash the insoluble part well; it will be a compound of zirconia, silica, potassa, and oxide of iron. Dissolve it in muriatic acid, and evaporate to dryness, to separate the silica. Re-dissolve the muriates of zirconia and iron in water; and to separate the zirconia which adheres to the silica, wash it with weak muriatic acid, and add it to the solution. Filter the fluid, and precipitate the zirconia and iron by pure ammonia; wash the precipitates well, and then treat the hydrates with oxalic acid, boiling them well together, that the acid may act on the iron, retaining it in solution whilst an insoluble oxalate of zirconia is formed. It is then to be filtered, and the oxalate washed, until no iron can be detected in the water that passes. The earthy oxalate is, when dry, of an opaline colour; after being well washed, it is to be decomposed by heat in a platinum crucible. Thus obtained, the zirconia is perfectly pure, but is not affected by acids. It must be re-acted on by potassa as before, and then washed until the alkali is removed. Afterwards dissolve it in muriatic acid, and precipitate by ammonia. The hydrate thrown down, when well washed, is perfectly pure, and easily soluble in acids.

The composition of zirconia has been estimated by Sir H. Davy (*Elements of Chemical Phil.* p. 361) at 37 zirconium + 8 oxygen. Berzelius says that it consists of 73.7 zirconium 26.3 oxygen; and from the experiments of Thomson, the number 40 is the equivalent of zirconium and 48 that of zirconia. These discrepancies must be done away by new experiments.

Sulphuret of Zirconium.—When zirconium and sulphur are heated in an atmosphere of hydrogen, a brown compound results, which is scarcely attacked by any of the acids except the hydrofluoric, which readily dissolves it with the disengagement of hydrogen.

iii. Glucina is also found in the *euclase*, a very scarce Peruvian mineral, composed, according to Berzelius, of

Silica	44.33
Alumina	31.83
Glucina	23.84
						<hr/> 190.00

To obtain glucina from either of these minerals, proceed as follows:—Reduce it to a fine powder, and fuse it with thrice its weight of pure potassa; dissolve in a dilute muriatic acid; evaporate to dryness; re-dissolve in water, and precipitate by carbonate of potassa. Dissolve this precipitate in sulphuric acid and add a little sulphate of potassa, and on evaporation crystals of alum will be obtained. These being separated, add excess of carbonate of ammonia to the residuary liquor, which will retain glucina in solution, but the remaining alumina will be precipitated; filter, and evaporate to dryness, and apply a red heat; glucina remains.

According to Berzelius, glucina is a compound of

1 proportional of glucinum	= 18
1 " oxygen	= 8
					<hr/>
Equivalent of oxide of glucinum	= 26

Section XL. YTTRIUM.

IN 1794, Professor Gadolin discovered a new earth in a mineral from the quarry of Ytterby in Sweden, to which Ekeberg, in 1797, gave the name of *Yttria*. The mineral has since been termed *Gadolinite*.

The following process for obtaining pure yttria is described by Vauquelin, in the 36th volume of the *Annales de Chimie*, p. 150. (Henry, ii. 648.)

Fuse the pulverized stone (called *Gadolinite*) with twice its weight of potassa; wash the mass with boiling distilled water, and filter. The filtered solution, which has a beautiful green colour, yields, during evaporation, a black pre-

precipitate of oxide of manganese. When this has ceased to appear, allow the liquor to stand; decant the clear part, and saturate with nitric acid. Let the insoluble part be also digested with extremely dilute nitric acid, which will take up the soluble earths only, and will leave undissolved the silica and oxide of iron. Let the two portions be mingled together, and evaporated to dryness; then re-dissolved and filtered; by which means any remains of silica and oxide of iron are separated. To obtain the yttria from the nitric solution, it would be sufficient, if no other earth were present, to precipitate it by carbonate of ammonia; but small portions of lime, and of oxide of manganese, are still present along with it. The first is separated by a few drops of carbonate of potassa; and the manganese by the cautious addition of hydro-sulphuret of potassa. The yttria is then to be precipitated by pure ammonia, washed abundantly with water, and dried*. It amounts to about 35, or, according to Berzelius, 45 per cent. of the weight of the stone. It has been found also to form about one-fifth of the weight of *yttrotalite*, and about one-twelfth of that of *ytthrocerite*.

Yttria is insipid, white, and without action on vegetable colours. Its specific gravity = 4.842. It is insoluble in water, but very retentive of it. Insoluble in pure alkalis, but readily soluble in carbonated alkalis. In carbonate of ammonia it is much less soluble than glucina. It forms salts which have a sweetish austere taste, and which have been little examined. They are decomposed by the pure alkalis and by lime and baryta. Oxalic acid and oxalate of ammonia throw down a white curdy precipitate from the solutions of yttria. Prussiate of potassa occasions in them a gray granular precipitate; phosphate of soda a white gelatinous one; and tincture of galls throws down brown flocculi.

The experiments, as yet published, upon the combinations of yttrium, do not enable us to determine its equivalent with accuracy. Berzelius has stated sulphate of yttria to consist of

* Nicholson's *Journal*, xviii. 77. Wöhler, to whom it was important to obtain pure yttria for the preparation of yttrium, remarked, that it was difficult to procure it quite free from sulphuric acid and potassa; from which sulphur and potassium were developed along with the metallic base.

equal weights of acid and base, which gives us the number 40 as the equivalent of yttria; and, supposing it a protoxide of yttrium, it will consist of

1	proportional yttrium	.	.	32	.	80
1	„ oxygen	.	.	8	.	20
				<hr/>		<hr/>
				40		100

From Dr. Thomson's experiments, the equivalent of yttrium is 34, and that of yttria 42.

CHAPTER VI*.

OF THE ASSAY AND ANALYSIS OF METALLIFEROUS COMPOUNDS.

THE chemical history of the metals, given in the preceding chapter, includes some brief account of the method of analyzing certain of their compounds; but upon this subject many details have necessarily been omitted in the different sections treating of the metals individually, in consequence of the numerous digressions that such discussion would have introduced: in the present chapter, therefore, it is proposed to describe such analytical processes as have not previously been adverted to, and are of frequent occurrence in the chemical laboratory; and likewise to point out the means of detecting impurities and adulterations in the various chemical products used in medicine and in the arts.

It is scarcely necessary to observe, that in all analytical operations distilled water is to be employed, and that the purity of the tests and re-agents must be previously ascertained: it is also convenient that they should be of some known degree of strength or concentration.

* It was my original intention considerably to have enlarged this chapter, by additional details relative to the apparatus and operations of analytical chemistry, but the publication of Mr. Faraday's excellent treatise on "Chemical Manipulation," has entirely superseded the necessity of such an undertaking. The analyses which I have quoted, and the processes which I have described, are exclusively intended for the use of the student; for an experienced operator scarcely requires the guidance of others, but invents, modifies, and applies his processes according to the particular exigencies of his investigations: the young analyst, on the contrary, by repeating the instructions of others, discovers their advantages and defects, and is led, under proper guidance, to adopt, modify, or reject them accordingly. These observations apply more strongly to the contents of the succeeding chapter "On the Analysis of Mineral Waters;" a branch of chemical art susceptible of infinite modifications, and for which no general directions can effectually be given; I have accordingly sketched an outline of proceeding, to which the student may resort merely as a practical exercise, and have referred to the least exceptionable authorities for his further instruction.

Among the most important apparatus of the chemical analyst, is a good balance ; he will generally find it convenient to employ two ; one, extremely delicate and capable of weighing from one-hundredth of a grain up to fifty grains (*Quarterly Journal*, xi. 280) ; the other, less sensible, but turning with one-tenth of a grain, when loaded with about an ounce in each scale. Larger balances are often requisite for weighing from one ounce to five or six pounds.

For the disintegration of very hard substances, mortars of hard steel, agate, or porphyry, are generally used, and the substance should be accurately weighed before and after pulverization, in order to ascertain whether it has suffered any increase from the abrasion of the mortar. The aggregation of many very hard stony substances may be diminished by heating them red-hot and quenching in water ; but care should be taken to ascertain the nature and quantity of any loss which they may sustain in this operation.

The proportion of any substance for an analysis varies, in ordinary cases, from 20 to 100 grains ; 50 grains is, generally speaking, a convenient quantity, and where there is no scarcity of the material, it is often advantageous to operate upon two or three portions at once, using each portion for ascertaining a distinct component part.

The crucibles employed in these analytical operations are either metallic, earthenware, or porcelain. Of the former, platinum, silver, and iron are chiefly useful ; platinum resists the action of the greater number of acids, but it is acted upon by alkaline substances ; pure silver is chiefly useful for alkaline fusions, but as it melts at a red heat, some care is requisite in its employment : for metallic substances, Hessian and Wedgwood crucibles are required ; the former, when well made, resist a very high heat without fusion, and bear sudden changes of temperature ; the latter are apt to crack, and should, therefore, be carefully heated, or placed in a Hessian crucible. It is often necessary to line a crucible with charcoal, which is most conveniently effected by mixing finely-powdered charcoal with a very little linseed-meal, and beating it into a stiff paste with a small addition of water ; the crucible is then dipped into water, and its interior lined to the

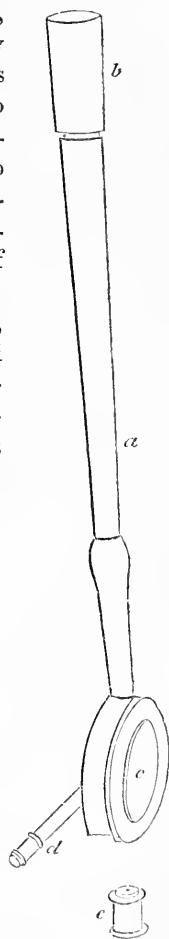
requisite thickness ; on applying heat, the linseed-meal burns, but the coating is not injured.

In the examination of mineral substances, the blowpipe is a most useful and necessary auxiliary to our other operations ; it affords a simple and convenient means of heating to a very high degree, and almost instantaneously, any substance sufficiently small to be enveloped in its flame ; and the experienced eye is thus frequently enabled to anticipate, with much precision, the nature of the substance submitted to experiment.

There are numerous forms of the blowpipe, among which, that represented in the annexed cut is perhaps the most convenient. It consists of a brass tube *a*, with an ivory mouth-piece *b* ; the other end of the tube terminates in a circular box, from which issues the small tube *d*, moveable in any direction round the centre *c*, by which any degree of obliquity may conveniently be given to the flame ; *e* is a brass jet which fits upon the tube *d*.

The following observations respecting the use of the blowpipe, and its action upon several substances, are extracted from Mr. Children's *Essay on Chemical Analysis* ; a work from which the student may derive much valuable information.

A continued stream of air is absolutely essential, to produce which, without fatigue to the lungs, an equable and uninterrupted inspiration must be maintained by inhaling air through the nostrils, whilst that in the mouth is forced through the tube by the compression of the cheeks. A little practice will make this operation easy, but at first considerable lassitude is generally experienced in the buccinator muscles. Upon this subject, see Faraday's *Manipulation*, sect. iv. After habit has rendered the operation familiar, a current may be kept up for ten or fifteen minutes, without inconvenience. A large wax candle supplies the best flame,



which being urged by the blast, exhibits two distinct figures; the internal flame is conical, blue, and well defined, at the apex of which the most violent degree of heat is excited: the external is red, vague, and undetermined, and of very inferior temperature to the former.

The substance to be submitted to the action of the blow-pipe, which should not be larger than a small pepper-corn, must be supported either on charcoal, or a slip of platina or silver foil, or be held in a pair of platina pincers. In the first case it may be placed in a cavity in the charcoal, and another piece laid over it to prevent its being carried off by the blast. The metallic supports are used when the subject of the experiment is intended to be exposed to the action of heat only, and might be altered by contact with the charcoal. If a very intense heat be required, the foil may be laid on charcoal. Salts and volatile substances are to be heated in glass tubes, closed at one end, and enlarged according to circumstances, so as to form small matrasses.

The exterior flame should first be directed on the substance, and when its action is known, then the interior blue flame. Notice should be taken, whether the matter decrepitates, splits, swells up, liquefies, boils, vegetates, changes colour, smokes, is inflamed, becomes obedient to the magnet, &c. *;

* M. Haüy has proposed the following ingenious method of rendering very weak magnetic attractions perceptible:—

If we conceive the needle to be removed a little from the plane of its magnetic meridian, its directing force will immediately tend to restore it, and with a power proportionate to the size of the angle which the needle makes with the magnetic meridian. Before any substance can act on the needle, it will have to overcome the directing force, as well as the friction at the point of suspension; obstacles which may prevent the effect of very slight attractions from being perceived. To diminish the force opposed to the action of the needle, M. Haüy places a magnetic bar at a certain distance from it, on the same level and in the direction of its axis, but with its poles situated contrary to those of the needle. If we suppose the magnetic bar to be placed to the south of the needle, the south pole of the magnet and the needle will be opposed to each other, and if the magnet be made to approach the needle, the latter will move on its centre towards one side or the other, till an equilibrium is produced between the mutual action of the magnet and needle, and that of the needle and the earth. Coulomb has shewn, that, in proportion as the needle deviates from its natural position, the increments of power necessary to produce equal effects, are in a decreasing ratio; so that when it has moved through nearly a quarter of a circle, a very small attractive power will be sufficient to influence it. When it is in this position, that is, nearly at right angles with the magnetic meridian, the needle is in its most sensible state;

when the action of heat alone has been ascertained, it will be necessary to examine what further change takes place, by fusing it with various fluxes, and also whether it be capable of reduction to the metallic state.

The three most useful fluxes are, the triple phosphate of soda and ammonia, subcarbonate of soda, and borax. These are to be kept ready pulverised, and when used, a sufficient quantity may be taken up by the moistened point of a knife; the moisture causes the particles to cohere, and prevents their being blown away, when placed on the charcoal. The flux must be melted into a clear bead, and the substance then placed on it, and submitted, first to the action of the exterior, and then to that of the interior, flame. The appearances which ensue must be observed; as,

1st. If the substance be dissolved, and whether with or without effervescence.

2nd. The transparency, and colour of the glass whilst cooling.

3rd. The same circumstances, when cold.

4th. The nature of the glass formed by the exterior flame.

5th. Also, by the interior flame.

6th. The particular appearances with each of the fluxes.

Subcarbonate of soda does not form a bead on charcoal, but with a certain degree of heat is absorbed; it must therefore be added in very small quantities, and a gentle heat used at first, which will promote combination without the absorption of the alkali. Some minerals combine readily with very small portions of soda, but difficultly if more be added, and are absolutely infusible with it in great excess; and when the substance has no affinity for this flux, it is absorbed by the charcoal, and no combination ensues.

When the mineral contains sulphur or sulphuric acid, the glass acquires a deep yellow colour, which by the light of a lamp appears red, as if produced by copper.

If the glass bead become opaque as it cools, so as to render

and is affected if any substance containing the most minute portion of iron be presented to it.

Haüy has by this method detected iron in several minerals where its presence was not suspected, or where it was supposed to exist in a state not liable to be affected by the magnet.—*Annals of Philosophy*, vol. xii. p. 117.

the colour indistinct, it should be broken, and a part of it mixed with more of the flux, till the colour becomes purer, and distinct. To make the colour more perceptible, the bead may be flattened whilst soft, or drawn out to a thread.

If it be wished to *oxidate* a metallic substance, combined with either of the fluxes, the glass is first heated intensely, and when fused, gradually withdrawn from the point of the blue flame, and the operation repeated as often as necessary, using a jet of large aperture. The addition of a little nitre also assists the oxidation. For the *reduction* of metallic oxides, the glass bead is to be kept in fusion on charcoal, as long as it remains on the surface and is not absorbed, that the metallic particles may collect into a globule. It is then to be fused with an additional quantity of soda, which will be absorbed by the charcoal, and the spot where the absorption has taken place strongly ignited by a tube with a small aperture. By continuing the ignition, the portion of metal which was not previously reduced will now be brought to the metallic state, and the process may be assisted by placing the bead in a smoky flame, so as to cover it with a soot that is not easily blown off.

The beads which contain metals frequently have a metallic splendour, which is most easily produced by a gentle, fluttering, smoky flame, when the more intense heat has ceased. With a moderate heat the metallic surface remains; and by a little practice it may generally be known whether the substance under examination contains a metal or not. But the glass of borax alone sometimes assumes externally a metallic appearance.

When the charcoal is cold, that part impregnated with the fused mass should be taken out with a knife, and ground with distilled water in an agate mortar. The soda will be dissolved; the charcoal will float, and may be poured off; and the metallic particles will remain in the water, and may be examined.

In this manner most of the metals may be reduced.

Action of the Blowpipe on the Earths and Metallic Oxides.

Baryta, when containing water, melts and spreads on the charcoal. Combined with sulphuric acid, it is converted, in the *interior* flame, into a sulphuret, and is absorbed by the

charcoal, with effervescence, which continues as long as it is exposed to the action of the instrument.

Strontia, if combined with carbonic acid, when held in small thin plates, with platinum forceps, in the *interior* flame, has its carbonic acid driven off, and on the side of the plate furthest from the lamp a red flame is seen, sometimes edged with green, and scarcely perceptible but by the flame of a lamp. Sulphate of strontia is reduced in the *interior* flame to a sulphuret; dissolve this in a drop of hydrochloric acid, add a drop of alcohol, and dip a thin slip of deal in the solution; it will burn with a fine red flame.

Lime.—The carbonate is easily rendered caustic by heat: it then evolves heat on being moistened, turns paper stained with turmeric brown, and is infusible before the blowpipe. The sulphate is easily reduced to a sulphuret, and possesses, besides, the property of combining with fluor spar at a moderate heat, forming a clear glass. The fluor should be rather in excess.

Magnesia produces, like strontia, an intense brightness in the flame of the blowpipe. A drop of a solution of cobalt being added to it, and then dried and strongly ignited, a faint flesh red colour, scarcely visible by the light of a lamp, is produced.

Magnesia may in this manner be detected in compound bodies, if they do not contain much metallic matter, or a quantity of alumina, exceeding that of the magnesia. Some inference, as to the proportion of the magnesia, may be drawn from the intensity of the colour produced.

All these alkaline earths, when pure, are readily fusible with the fluxes, into a clear, colourless glass, without effervescence; but on adding a further quantity of the earth, the glass becomes opaque.

Alumina combines more slowly with the fluxes than the preceding earths, and forms a clear glass, which does not become opaque. But the most striking character of alumina is the bright blue colour it acquires from the addition of a drop of nitrate of cobalt, after having been dried and ignited for some time. It may thus be detected in compound minerals where the metallic substances are not in great proportion, nor the quantity of magnesia large.

The following, according to Berzelius, is a ready method of

discovering *lithia* in any mineral supposed to contain it; it is founded on the facility with which that alkali attacks platinum.

Take a morsel of the mineral, about the size of a pin's head, or a small quantity of it reduced to fine powder, and heat it with an excess of soda, on a slip of platinum foil before the blowpipe, and keep it red hot for about two minutes. The stone will be decomposed, the soda will expel the lithia from its combination, and the excess of alkali, becoming fluid at this temperature, will spread over the surface of the foil, and envelope the decomposed mass. The platinum round the fused alkaline mass assumes a dark colour, deep and extensive in proportion to the quantity of lithia in the mineral. The platinum beneath the alkali is not oxidated, but only in those parts where it is in contact both with the air and the lithia. Potassa destroys the action of platinum on the lithia, if it be not in considerable quantity. The metal recovers its brilliancy after being well washed with water and heated to redness.—*Ann. de Chim.* vol. x. p. 104, note.

Metallic Oxides and Acids.

Arsenic flies off accompanied by its characteristic smell, resembling garlic. When large pieces of white arsenic are heated on ignited charcoal, no smell is perceived. To produce this effect, the white oxide must be reduced by being mixed with powdered charcoal. If arsenic be suspected in a solution, it may be discovered by dipping into it a piece of pure and well-burnt charcoal, which is afterwards to be dried and ignited.

Chromium.—Its green oxide exhibits the following properties: it is fusible with microcosmic salt (phosphate of soda and ammonia) in the interior flame, into a glass which at the instant of its removal from the flame is of a violet hue, approaching more or less to dark blue or red, according to the proportion of the chromium. After cooling, the glass is bluish-green, but less blue than copper glass. In the exterior flame the colour becomes brighter, and less blue than the former. With borax it forms a bright yellowish or yellow red glass in the exterior flame; and in the interior flame this becomes darker and greener, or bluish-green.

Molybdic Acid melts by itself upon the charcoal with ebullition, and is absorbed. In a platinum spoon it emits white fumes, and is reduced in the interior flame to molybdous acid, which is blue, but in the exterior flame it is again oxidated and becomes white. With microcosmic salt, in the exterior flame, a small proportion of the acid gives a green glass, which by gradual additions of the acid passes through yellow green to reddish, brownish, and hyacinth brown, with a slight tinge of green. In the interior flame the colour passes from yellow-green, through yellow-brown, and brown-red, to black; and if the proportion of acid be large, it acquires a metallic lustre, like the sulphuret, which sometimes remains after the glass has cooled. Molybdic acid is but sparingly dissolved by borax. In the exterior flame the glass acquires a gray-yellow colour. In the interior flame black particles are precipitated from the clear glass, leaving it almost colourless when the quantity of molybdenum is small, and blackish when the proportion is large. If, to a glass formed of this acid and microcosmic salt a little borax be added, and the mixture fused in the exterior flame, the colour becomes instantly reddish-brown: in the interior flame the black particles are also separated, but in smaller quantity. By long-continued heat the colour of the glass is diminished, and it appears yellower by the light of a lamp than by day-light. This acid is not reduced by soda in the interior flame.

Tungstic Acid becomes upon charcoal at first brownish-yellow, is then reduced to a brown oxide, and lastly, becomes black without melting or smoking. With microcosmic salt it forms in the interior flame a pure blue glass, without any violet tinge; in the exterior flame this colour disappears, and appears again in the interior. With borax, in the internal flame, and in small proportion, it forms a colourless glass, which, by increasing the proportion of acid, becomes dirty gray, and then reddish. By long exposure to the external flame it is rendered transparent, but as it cools it becomes muddy, whitish, and changeable into red when seen by day-light. It is not reduced.

Oxide of Columbium undergoes no change by itself, but is readily fused with microcosmic salt and with borax, into a clear colourless glass, from which the oxide may be precipitated by

heating and cooling it alternately. The glass then becomes opaque, and the oxide is not reduced.

Oxide of Titanium becomes yellowish when ignited in a spoon, and upon charcoal dark brown. With microcosmic salt it gives in the interior flame a fine violet-coloured glass, more tending to blue than that from manganese. In the exterior flame this colour disappears. With borax it gives a dirty hyacinth colour.

Oxide of Cerium becomes red-brown when ignited. When the proportion is small, it forms with the fluxes a clear, colourless glass, which by increasing the proportion of oxide becomes yellowish-green while hot. With microcosmic salt, if heated a long time in the internal flame, it gives a clear colourless glass.

With borax, under similar circumstances, it gives a faint yellow-green glass while warm, but is colourless when cold. Exposed again for some time to the external flame, it becomes reddish-yellow, which colour it partly retains when cold. If two transparent beads, one of the compound with microcosmic salt, the other with borax, be fused together, the triple compound becomes opaque and white. The oxide is volatile.—See Thomson's *Chemistry*, vol. i. p. 408, 5th edition.

Oxide of Uranium.—The yellow oxide by ignition becomes green or greenish-brown. With microcosmic salt in the interior flame it forms a clear yellow glass, the colour of which becomes more intense when cold. If long exposed to the exterior flame, and frequently cooled, it gives a pale yellowish, red-brown glass, which becomes greenish as it cools. With borax in the interior flame, a clear, colourless, or faintly green glass is formed, containing black particles, which appear to be the metal in its lowest state of oxidation. In the exterior flame this black matter is dissolved, if the quantity be not too great, and the glass becomes bright yellowish-green, and after further oxidation yellowish-brown. If brought again into the interior flame, the colour gradually changes to green, and the black matter is again precipitated, but no further reduction takes place.

Oxide of Manganese gives with microcosmic salt, in the exterior flame, a fine amethyst colour, which disappears in the interior flame. With borax it gives a yellowish hyacinth-red

glass. When the manganese, from its combination with iron, or any other cause, does not produce a sufficiently intense colour in the glass, a little nitre may be added to it while in a state of fusion, and the glass then becomes dark violet while hot, and reddish violet when cool. It is not reduced.

Oxide of Tellurium, when gently heated, becomes first yellow, then light red, and afterwards black. It melts and is absorbed by the charcoal, and is reduced with a slight detonation, a greenish flame, and a smell of horse-radish. Microcosmic salt dissolves it without being coloured.

Oxide of Antimony is partly reduced in the exterior flame, and spreads a white smoke on the charcoal. In the interior flame it is readily reduced, either alone, or with the addition of soda. With microcosmic salt and with borax it forms a hyacinth-coloured glass. Metallic antimony, when ignited on charcoal, becomes covered with radiating acicular crystals of white oxide. Sulphuret of antimony melts on charcoal, and is absorbed.

Oxide of Bismuth melts readily in a spoon to a brown glass, which becomes brighter as it cools. With microcosmic salt it forms a gray-yellow glass, which loses its transparency, and becomes pale when cool. Add a further proportion of oxide, and it becomes opaque.

With borax it forms a gray glass, which decrepitates in the interior flame, and the metal is reduced and volatilized. It is readily reduced by itself on charcoal.

Oxide of Zinc becomes yellow when heated, but whitens as it cools. A small proportion forms with microcosmic salt and with borax a clear glass, which becomes opaque on increasing the quantity of oxide. A drop of nitrate of cobalt being added to the oxide and dried and ignited, it becomes green. With soda in the interior flame it is reduced, and burns with its characteristic flame, depositing its oxide upon the charcoal. By this process zinc may be easily detected even in the automalite. Mixed with oxide of copper, and reduced, the zinc will be fixed, and brass obtained. But one of the most unequivocal characters of the oxide of zinc is, to dissolve it in vinegar, evaporate the solution to dryness, and expose it to the flame of a lamp, when it will burn with its peculiar flame.

Oxide of Cadmium is orange yellow, not volatile, and easily

reduced ; it gives no colour to borax.—*Ann. de Chim. et Phys.* tom. viii. p. 100.

Oxide of Iron produces with microcosmic salt, or borax in the exterior flame, when cold, a yellowish glass, which is blood-red while hot. The protoxide forms with these fluxes a green glass, which, by increasing the proportion of the metal, passes through bottle-green to black, and is opaque. The glass from the peroxide becomes green in the interior flame, and is reduced to protoxide, and becomes attractable by the magnet. When placed on the wick of a candle, it burns with the crackling noise peculiar to iron.

Oxide of Cobalt becomes black in the exterior, and gray in the interior flame ; a small proportion forms with microcosmic salt and with borax a blue glass, that with borax being the deepest. By transmitted light the glass is reddish. By further additions of the oxide, it passes through dark blue to black. The metal may be precipitated from the dark blue glass by inserting a steel wire into the mass while in fusion. It is malleable if the oxide has been free from arsenic, and may be collected by the magnet, and is distinguished from iron by the absence of any crackling sound when placed on the wick of a candle.

Oxide of Nickel becomes black at the extremity of the exterior flame, and in the interior greenish gray. It is dissolved readily, and in large quantity, by microcosmic salt. The glass, while hot, is a dirty dark red, which becomes paler and yellowish as it cools. After the glass has cooled, it requires a large addition of the oxide to produce a distinct change of colour. It is nearly the same in the exterior and interior flame, being slightly reddish in the latter. Nitre added to the bead makes it froth, and it becomes red-brown at first, and afterwards paler. It is easily fusible with borax, and the colour resembles the preceding. When this glass is long exposed to a high degree of heat in the interior flame, it passes from reddish to blackish and opaque, then blackish-gray, and transparent ; then paler reddish-gray, and clearer ; and lastly, transparent, and the metal is precipitated in small white metallic globules.

The red colour seems here to be produced by the entire fusion or solution of the oxide, the black by incipient reduc-

tion, and the gray by the minute metallic particles before they combine and form small globules. When a little soda is added to the glass formed with borax, the reduction is more easily effected, and the metal collects itself into one single globule. When this oxide contains iron, the glass retains its own colour while hot, but assumes that of the iron as it cools.

Oxide of Tin, in form of hydrate, and in its highest degree of purity, becomes yellow when heated, then red, and when approaching to ignition black. If iron or lead be mixed with it, the colour is dark brown when heated. These colours become yellowish as the substance cools. Upon charcoal in the interior flame, it becomes and continues white; and if originally white, and free from water, it undergoes no change of colour by heating. It is very easily reduced without addition, but the reduction is promoted by adding a drop of solution of soda or potassa.

Oxide of Lead melts, and is very quickly reduced, either without any addition, or when fused with microcosmic salt or borax. The glass not reduced is black.

Oxide of Copper is not altered by the exterior flame, but becomes protoxide in the interior. With both microcosmic salt and borax it forms a yellow-green glass while hot, but which becomes blue-green as it cools. When strongly heated in the interior flame, it loses its colour, and the metal is reduced. If the quantity of oxide be so small that the colour be not perceptible, its presence may be detected by the addition of a little tin, which occasions a reduction of the oxide to protoxide, and produces an opaque red glass. If the oxide has been fused with borax, this colour is longer preserved; but if with microcosmic salt, it soon disappears by a continuance of heat. The copper may also be precipitated upon iron, but the glass must be first saturated with iron. Alkalis or lime promote this precipitation. If the glass, containing copper, be exposed to a smoky flame, the copper is superficially reduced, and the glass covered while hot with an iridescent pellicle, which is not always permanent after cooling. It is very easily reduced by soda. Salts of copper, when heated before the blowpipe, give a fine green flame.

Oxide of Mercury, before the blowpipe, becomes black, and

is entirely volatilized. In this manner its adulteration may be discovered.

The other metals may be reduced by themselves, and may be known by their own peculiar characters. — Thomson's *Annals*, No. lxi. p. 42, et seq.

Although many of the analyses in the following sections have been conducted in the laboratory of the Royal Institution, and are therefore the results of actual experiment, there are difficulties in their performance, which practice alone will enable the student to overcome; and fallacies, to which, even with extensive experience, he will still find himself liable. Among the latter, I cannot help adverting to those attractions of the metallic oxides for each other, which have been but little studied, but which often present serious difficulties to the proceedings of the analyst: where, for instance, several earths are held in the same solution, it is extremely difficult to effect their complete separation by the agency of those precipitants, which are generally regarded as throwing down only one of them: in the same way, although water occasions no precipitate in permuriate of tin, but throws down the oxide from permuriate of antimony, yet if the permuriates be mixed, it is found that the precipitate by water contains a very notable proportion of peroxide of tin; and many similar cases might be adduced.

The practice of submitting substances of known composition to analysis, cannot be too strongly recommended to the chemical student; it makes him acquainted with the mutual actions and habitudes of a number of bodies, which experience can alone teach, and gives a dexterity of manipulation, and an accuracy in conducting experimental inquiries, of which he will find the value when subsequently in the pursuit of original investigations.

Section I. OF THE COMPOUNDS OF POTASSIUM.

PURE Potassa should be perfectly soluble in twice its weight of water, and the solution should not effervesce upon the addition of a few drops of nitric acid, but remain undisturbed and transparent.

If nitric acid cause an effervescence in the solution of potassa, it indicates *carbonic acid* ; if a gelatinous precipitate not soluble in slight excess of the acid, it is *silica* ; if a precipitate soluble in slight excess of acid, it is *alumina*.

The presence of *lime* in solution of caustic potassa is shown by neutralizing it by nitric acid, filtering, if necessary, and adding oxalate of ammonia, which causes a white cloud ; or by the production of a precipitate of carbonate of lime upon adding solution of bicarbonate of potassa.

Baryta water should occasion no turbidness in a solution of pure potassa ; if it occasion a precipitate soluble with effervescence in nitric acid, it announces *carbonic acid* ; if insoluble, *sulphuric acid*.

Chlorate of Potassa is sometimes mixed with a little of the *chloride of potassium*, which is shown by the addition of solution of nitrate of silver occasioning a precipitate, which it does not in the solution of the pure chlorate.

Nitrate of Potassa.—The quantity of pure nitre in a given portion of the rough salt may be learned with tolerable accuracy by the following process :—

Purification of Nitre.—7 lbs. of rough nitre are accurately weighed, and then dissolved by heat in 21 parts of water ; when boiling, the scum is removed until no more rises, and then the solution is allowed to settle for ten minutes or longer. In this way nearly all the dirt falls down, and the clear solution being poured off, is passed through a filter of tow into a pan, and set aside to crystallize ; the dirt left behind is added to the scum, and both being diluted, are filtered through paper, and the clear solution preserved. Next day the crystals formed in the pan are separated and put into funnels to drain, and the mother liquor with the filtered solution from the scum,

&c., are further evaporated, and again left to crystallize. On the second evaporation, impurities generally separate from the solution; these are sometimes oxide of iron, or sulphate of lime, but most frequently common salt and nitrate of soda. The two first are easily separated by filtration; the third is best separated by evaporating the solution considerably, until much salt has been deposited, and then pouring the whole upon a filter of tow; the common salt will remain on it, and should be washed by water to separate the nitre, which water should be added to the liquor, and the whole then brought to the crystallizing point. When cold, the crystals deposited by this solution are to be separated, and more salt separated as before, until the mother liquor is divided into common salt and nitre. It frequently happens that the crystals from the two or three last evaporations are coloured or contaminated by the adhesion of common salt, sulphate of lime, &c.; in this case, they should be re-dissolved and re-crystallized with the same precautions as before. Care should be taken in drying the crystals, especially when small or when hastily formed, that no water remain in the interstices or cleavages between them.

Solution of pure nitre is not rendered turbid either by nitrate of silver or nitrate of baryta.

Gunpowder.—To analyze this compound, boil it with four parts of water, edulcorate the residue, dry it at 212° , and weigh; the loss indicates the nitre. The dry residue, composed of charcoal and sulphur, may be decomposed by spreading it upon an earthen plate, and burning off the sulphur at the lowest possible heat; the charcoal will remain, still however retaining a little sulphur. A more accurate process consists in introducing the mixture into a small retort furnished with a stop-cock, exhausted, and filled with chlorine; heat applied volatilizes the chloride of sulphur and leaves the charcoal, which may be washed, dried, and weighed. A third mode of analysing gunpowder consists in separating the nitre by water, evaporating to dryness, and fusing the salt. To obtain the sulphur, 5 grains of the powder, 5 of carbonate of potassa, 5 of nitre, and 20 of pure common salt, are to be intimately mixed, and placed on the fire in a platinum vessel; the sulphur is slowly acidified, and when the mass becomes white it is dissolved in water, saturated with nitric or muriatic acid,

and muriate of baryta added as long as it occasions a precipitate: the sulphate of baryta thrown down is then collected, washed, and ignited, and being carefully weighed, indicates the quantity of sulphur contained in the gunpowder, by the usual computation. (*Ann. de Chim.* xvi. 437.)

Carbonate of Potassa.—Dr. Henry has given the following directions for ascertaining the quantity of real alkali contained in the rough alkalis of commerce; the process depends upon their saturating power in respect to an acid of known density, and the principle of the analysis has been already adverted to; his directions, however, are of such practical utility, that I have, with his permission, transcribed them.

“Provide a tube, nine inches and a half long and three-fourths of an inch internal diameter, provided with a lip for the convenience of pouring, and a glass foot to support it.

“A tube of this kind holds 1000 grains of water, and (which is desirable) a little more. To graduate it, weigh into it 100 successive portions of distilled water at 60° Fahrenheit, of ten grains each; or, if the tube be of equal bore throughout, it may be sufficient to weigh into it ten successive portions of water of 100 grains each, dividing each of the intermediate spaces into ten parts by a pair of compasses. When 1000 grains of water have been weighed into the tube, a line may be drawn with a file, which may be marked 0, the tenth below this 10, and so on.

“The test acid, which I prefer, is made by diluting one part of oil of vitriol of commerce, of specific gravity 1.849, with four parts of water; consequently, one-fifth part of its weight is concentrated oil of vitriol, and its specific gravity is, as nearly as possible, 1.141. Acid of this strength does not, on farther dilution, give out any heat, that can be a source of inaccuracy.

“When an alkali is to be examined, find, by the Scale of Equivalents, how many grains of oil of vitriol are required to neutralize 100 grains of what may be considered the proper alkaline ingredient of the substance in question. This, in *pearlash*, is subcarbonate (carbonate) of potash; in *potash*, pure potash; in *barilla*, or *kelp*, dry subcarbonate (carbonate) of soda. Let us take pearlash as an example. On referring to the scale, we find that 100 grains of subcarbonate of potash are equiva-

lent to 71 grains of concentrated oil of vitriol *. Put, therefore, into the test tube a quantity of the dilute acid containing 71 grains of concentrated acid, viz., 355 grains; and to spare the trouble, on any future occasion, of weighing the acid, let a line be drawn with a file on the blank side of the tube, at the level of the acid liquor, which may be marked *Equiv. of Subc. Pot.*

“ Fill up the tube with water to the line marked 0, and mix the acid and water completely by pouring them into a lipped glass vessel; stirring with a glass rod; and then returning them into the tube. Now as the whole 100 measures contain a quantity of oil of vitriol equivalent to 100 grains of subcarbonate of potash, it is obvious that each measure of the liquor in the tube is adequate to the neutralization of one grain of the subcarbonate.

“ Let 200 grains, taken out of a fair average specimen of the pearlash to be examined, be dissolved in two ounce measures of warm distilled water; filter the solution; and wash the filter with two ounces more of water, which is best applied to the margin of the paper by means of a dropping bottle. Add the washings to the solution; and having mixed the whole together, pour one-half into a tumbler or goblet, reserving the other half for a repetition of the experiment if necessary.

“ To the liquor in the glass goblet, add the diluted acid very gradually, making the additions more and more slowly towards the last. As soon as the point of neutralization is attained, which will be shown by the cessation of a change of colour in slips of litmus and of turmeric paper, dipped, from time to time, into the liquor, no more acid must be added. It is proper, however, the operator should be aware that there will often be an apparent excess of test acid, in consequence of the carbonic acid, which is disengaged, acting on the litmus paper. To avoid this source of error, it is advisable, towards the last, to warm the liquor, by setting the glass containing it for half an hour near the fire, and while thus warmed, to add very cautiously the rest of the acid required for saturation. This point being attained, the number on the test-tube, at the level of the acid remaining in it, shews at once, without any

* Dr. Ure makes it 70.4.—*Journ. of Science*, iv. 119.

calculation, how much *per cent.* of subcarbonate of potash is contained in the pearlash under examination. In the samples I have tried, it has generally been about 80 *per cent.*

“ In operating on barilla, kelp, or any variety of the mineral alkali, the process is exactly the same, except that as 93 * of oil of vitriol are equivalent to 100 of subcarbonate of soda, we must take $93 \times 5 = 465$ grains, of sulphuric acid, of density 1.141. This may be marked on the tube, *Equiv. of Subc. of Soda*. In a similar manner, we may mark on the tube the equivalent of *pure potash*, viz., 520 grains of the above diluted acid; and that of *pure soda*, 783 grains; with any other equivalents, that may be likely to be of use.

“ Having ascertained the proportion of subcarbonate of potash in any sample of pearlash, it is easy to find, by the sliding scale, its equivalent quantity of pure or caustic potash. Thus, supposing the pearlash to contain 80 *per cent.* of subcarbonate, that number being set to subcarbonate of potash on the scale, the equivalent in pure potash is at once seen to be 55.

“ To determine, by the same graduated tube, the strength of *any acid* whose equivalent is known (which is the reverse of the foregoing process), we must put 100 grains of the acid, with a sufficient quantity of water, into a goblet; and use, for saturating it, its equivalent of any alkali. For example, 100 grains of concentrated oil of vitriol requiring for saturation 108 grains of *dry* subcarbonate of soda, dissolve the latter quantity of alkali in water sufficient to make up 100 measures of solution in the tube; then pour the alkaline solution to the acid liquor, till the latter is neutralized; and the number of measures, which have been expended, exactly denote the strength of the acid.

“ It may sometimes be desirable to know the proportion, not of concentrated or of real acid, but of acid of some inferior degree of density, in a specimen of acid. The method of doing this will best be explained by an example. Suppose that we wish to know the equivalent, in muriatic acid of sp. gr. 1.160, to 100 grains of the same acid of sp. gr. 1.074; find, by the alkaline test, or by referring to the table of the strength of muriatic acid, how much real acid 100 grains of both those

* According to Dr. Ure, 91.4 is the true equivalent.—*Journal of Science*, &c., iv. 119.

acids contain. In acid of sp. gr. 1.160, it will be 23.4 *per cent.*; in acid of sp. gr. 1.074, it will be 11. Then $23.4 : 100 :: 11 : 47$. Therefore 47 grains of muriatic acid, of sp. gr. 1.160, are equivalent, in acidity, to 100 of sp. gr. 1.074.

“No chemical operation can be more simple, or more easily managed, than the measurement of the strength of alkalis by acid liquors, and of acids by alkaline ones, in the way which has been described. The test-tube, which is the only instrument required for that purpose, may be had at any glass-house, and may easily be graduated by any person who will take the necessary pains. When once accurately prepared, it will be found also useful for a variety of other purposes, which will readily present themselves to the practical chemist.”

The *purified Carbonate of Potassa* of the shops should be perfectly soluble in twice its weight of cold water. It often contains *silica, sulphate of potassa, chloride of potassium, and carbonate of lime*. To detect these, dissolve a hundred grains in excess of nitric acid diluted with eight parts of water; the silica, if any be present, remains undissolved, or may be rendered insoluble by evaporation: separate the solution into three equal parts; to the first, add nitrate of baryta, which causes a precipitate of sulphate; collect, wash, and dry it; 100 parts are equivalent to 74 of sulphate of potassa: to the second, add nitrate of silver; 100 grains of the precipitate, washed and dried at a dull red heat, are equivalent to 52 of chloride of potassium: to the third, add oxalate of ammonia, and dry the edulcorated precipitate at a heat of 300° ; 100 parts are equal to 77 of carbonate of lime.

There are a few *mineral substances* which contain potassa; it was first detected in the *leucite* by Klaproth, whose analysis of that mineral may be advantageously consulted by the student. (*Analytical Essays*, i. 348.) It consists of

Silica	53.750
Alumina	24.625
Potassa	21.350
	<hr/>
	99.725

There are three modes of analysis which may be practised upon such minerals; they may either be directly acted upon

by acids : or fused with baryta, and afterwards submitted to acid solution ; or fused with oxide of lead.

A. 100 grains of leucite in very fine powder were digested for six hours in muriatic acid, which was then decanted off and the residue washed upon a filter, the washings being mixed with the solution. The residue weighed 60 grains. (*a*.)

B. The muriatic solution was supersaturated with pure ammonia, which occasioned a bulky brownish precipitate (*b*), which was collected, washed, and dried ; it amounted to 12.5 grains.

C. Carbonate of ammonia produced no change in the last-mentioned filtrated liquor, which was therefore evaporated to dryness, and the residue exposed to a red heat in a platinum crucible ; it was then completely re-dissolved in water, and again evaporated to dryness ; it had the characters of chloride of potassium (*c*), and weighed 41 grains.

D. The residue *a* A was fused with three parts of potassa in a silver crucible, the fused mass dissolved in water, supersaturated with muriatic acid, evaporated to dryness, and again digested in water ; there remained 58.5 grains of dry and pure silica.

B. The precipitate *b* B was entirely soluble in pure solution of potassa, with the exception of a trace of oxide of iron. Being again thrown down by muriate of ammonia, it was found to be pure alumina.

E. The chloride of potassium *c* C was decomposed in a platinum crucible by sulphuric acid, and it afforded 48 grains of sulphate of potassa, which is equivalent to 26 of potassa.

The result of this analysis differs in the proportions of the components from that of Klaproth ; it may be stated as follows :—

	Grains.
Silica, A <i>a</i>	58.5
Alumina with a trace of iron, B <i>b</i> and E	12.5
Potassa, C <i>c</i> F	26.
Loss	3.
	<hr/> 100.

The analysis of an alkaline mineral by the aid of Baryta is shown further on.

When oxide of lead is used, the mineral in powder may be

fused in a platinum crucible with three or four parts of nitrate of lead. The fused mass may then be boiled in diluted nitric acid, which leaves the silica; this being separated, sulphuric acid is added to throw down the lead, the entire separation of which is ensured by the test of sulphuretted hydrogen. The acid solution is then boiled with excess of carbonate of ammonia, and the precipitate analyzed by the usual methods; the remaining liquid is then evaporated to dryness, the residue calcined and weighed; it contains the alkali in the state of sulphate, sometimes a little acid, and almost always magnesia: the other steps of the analysis are sufficiently indicated elsewhere. (*Ann. de Chim. et Phys.* xvii. 28.)

It may here be remarked, that the existence of potassa, soda, and lithia in minerals, is generally first indicated by the great apparent loss which is sustained upon collecting and weighing their precipitable components: thus, if in any case of analysis we lose, upon the aggregate weight of the precipitates, more than 2 or 3 *per cent.*, we may suspect the existence of the fixed alkalis, and direct our attention accordingly to their detection. It also generally happens, that minerals which contain any considerable proportion of fixed alkaline substances, are remarkable for the facility with which they enter into fusion before the blowpipe.

Section II. OF THE COMBINATIONS OF SODIUM.

PURE SODA may be tested in the same way as pure potassa. The presence of *potassa* in soda may be detected by neutralizing it with muriatic acid, and adding to the solution, muriate of platinum, which forms a buff-coloured precipitate if potassa be present. The solutions should be concentrated.

Chloride of Sodium.—The usual impurities of sea-salt are *muricates of magnesia and lime*. Dissolve 100 grains in an ounce of water, and add carbonate of ammonia, which throws down carbonate of lime, 100 parts of which, washed and dried at 300°, are equivalent to 110 of dry muriate of lime (chloride

of calcium). Boil the filtered liquor nearly to dryness, and carbonate of magnesia falls, of which 100 parts are equal to about 134 of dry muriate of magnesia. (Henry, *Phil. Trans.*, 1810, p. 109.)

Sulphate of Soda.—This salt, in the form of crystals, may be analyzed as follows: Weigh off 100 grains, and introduce it into a platinum crucible, previously weighed; place it in a sand heat, and *gradually* give it a dull red heat for half an hour; when cold, ascertain the loss of weight, which is *water of crystallization* (*a.*) Pour two ounces of water upon the dry salt, and when perfectly dissolved add solution of nitrate of baryta as long as it occasions any precipitate; edulcorate, dry, and weigh the sulphate of baryta thrown down (*b.*), of which 100 parts indicate 34 of sulphuric acid. The filtered liquor contains the soda, now in the state of nitrate, and any excess of nitrate of baryta that might have been added: evaporate it to dryness, expose the residue to a red heat for half an hour in a platinum crucible, by which the acid will be expelled, and a mixture of soda and baryta remain; pour upon it dilute sulphuric acid, which forms sulphate of soda and sulphate of baryta; the latter, being insoluble, is separated by filtration; the filtered solution of regenerated sulphate of soda should afford, on evaporation and expulsion of water as above directed, a quantity of sulphate, exactly equal to that of the process (*a.*). Thus it will be found that 100 grains of sulphate of soda in crystals, afford of

Water	56.00
Sulphuric acid	24.75
Soda	19.25

Sulphate of soda is seldom sophisticated: it should not change the colour of litmus or turmeric; it sometimes contains a little iron, which interferes with some of its pharmaceutical uses; this may be detected by adding tincture of galls to the aqueous solution of the salt, slightly acidulated by nitric acid, when it occasions a black cloud. Sea salt is discovered in solution of sulphate of soda, by the addition of sulphate of silver; salts of lime are shown by the precipitate of carbonate of lime, occasioned by carbonate of ammonia. Sulphate of potassa is recognized by its sparing solubility.

Carbonate of Soda.—The analysis of kelp and barilla has been above referred to—(page 277.)

The carbonate of soda of the shops (*sodæ subcarbonas* of the *Pharmacopœia*) often contains *sulphate of soda* and *sea salt*; to discover these, saturate a given weight of the salt with pure dilute nitric acid, and divide the solution into two parts: to one add nitrate of baryta, which gives a precipitate of sulphate of baryta; to the other add nitrate of silver, which throws down chloride of silver, of which 100 parts, properly washed and dried, are equal to 41 of sea salt.

If carbonate of soda contain *carbonate of potassa*, its presence is shown by adding to a saturated solution of the carbonate, a saturated solution of tartaric acid *in excess*; a precipitation of crystalline grains of bitartrate of potassa ensues if potassa be present.

Bicarbonate of Soda is frequently mixed with sesqui-carbonate and carbonate of soda; and it is difficult to detect the proportion of these by any other means than the quantity of carbonic acid evolved from a given weight. The composition of the bicarbonate is given above.

Borate of Soda, or borax, is sometimes adulterated by common salt, and by alum. To detect these, dissolve a portion of the salt in 20 parts of water, and *add slight excess of nitric acid*. Test this solution by nitrate of silver for the discovery of sea salt; and by nitrate of baryta for sulphuric acid.

There are several minerals which contain soda; the following analysis of the *sodalite*, by Dr. Thomson, may be taken as an instance of one mode of proceeding in these cases.—*Phil. Mag.*, xxxvii. p. 303; or, *Transactions of the Royal Society of Edinburgh*.

“ 100 grains of the mineral, reduced to a fine powder, were mixed with 200 grains of pure soda, and exposed for an hour to a strong red heat in a platinum crucible. The mixture melted, and assumed, when cold, a beautiful grass-green colour. When softened with water, the portion adhering to the sides of the crucible, acquired a fine brownish yellow. Nitric acid being poured upon it, a complete solution was obtained. Suspecting, from the appearance which the fused mass assumed, that it might contain chromium, I neutralized the solution as nearly as possible with ammonia, and then poured into it a recently prepared nitrate of mercury. A white precipitate fell, which being dried and exposed to a heat

rather under redness, was all dissipated, except a small portion of gray matter, not weighing quite 0.1 grain. This matter was insoluble in acids, but became white. With potash it fused into a colourless glass. Hence I consider it as silica. This experiment shows that no chromium was present. I was at a loss to account for the precipitate thrown down by the nitrate of mercury. But Mr. Allan having shown me a letter from Ekeberg, in which he mentions that he had detected muriatic acid in sodalite, it was easy to see that the whole precipitate was calomel. The white powder weighed 26 grains, indicating, according to the analysis of Chenevix, about three grains of muriatic acid.

“ The solution, thus freed from muriatic acid, being concentrated by evaporation, gelatinized. It was evaporated nearly to dryness, the dry mass digested in hot water, acidulated with nitric acid, and poured upon the filter, was washed, dried, and heated to redness. It weighed 37.2 grains, and was silica. The liquor which had passed through the filter was supersaturated with carbonate of potash, and the copious white precipitate which fell, collected by the filter, and boiled, while yet moist, in potash-*lie*. The bulk diminished greatly, and the undissolved portion assumed a black colour, owing to some oxide of mercury with which it was contaminated. The potash *lie* being passed through the filter, to free it from the undissolved matter, was mixed with a sufficient quantity of sal-ammoniac. A copious white precipitate fell, which being collected, washed, dried, and heated to redness, weighed 27.7 grains. This powder being digested in sulphuric acid, dissolved except 0.22 grain of silica. Sulphate of potash being added, and the solution set aside, it yielded alum crystals to the very last drop. Hence the 27.48 grains of dissolved powder were alumina.

“ The black residue, which the potash *lie* had not taken up, was dissolved in diluted sulphuric acid. The solution being evaporated to dryness, and the residue digested in hot water, a white soft powder remained, which, heated to redness, weighed 3.6 grains, and was sulphate of lime, equivalent to about 2 grains of lime.

“ The liquid from which the sulphate of lime was separated, being exactly neutralized by ammonia, succinate of ammonia was dropped in, a brownish-red precipitate fell, which, being

heated to redness in a covered crucible, weighed one grain, and was black oxide of iron.

“ The residual liquor being now examined by different reagents, nothing further could be precipitated from it. The liquid from which the alumina, lime, and iron, had been separated by carbonate of potash, being boiled for some time, let fall a small quantity of yellow-coloured matter. This matter being digested in diluted sulphuric acid, partly dissolved with effervescence, but a portion remained undissolved, weighing one grain. It was insoluble in acids, and with potash melted into a colourless glass. It was, therefore, silica. The sulphuric acid solution being evaporated to dryness, left a residue which possessed the properties of sulphate of lime, and which weighed 1.2 grains, equivalent to about 0.7 grain of lime.

“ The constituents obtained by the preceding analysis being obviously defective, it remained to examine whether the mineral, according to the conjecture of Bournon, contained an alkali. For this purpose 100 grains of it, reduced to a fine powder, and mixed with 500 grains of nitrate of barytes, were exposed for an hour to a red heat in a porcelain crucible. The fused mass was softened with water, and heated with muriatic acid. The whole dissolved except 25 grains of a white powder, which proved on examination to be silica. The muriatic acid solution was mixed with sulphuric acid, evaporated to dryness, the residue digested in hot water, and filtered, to separate the sulphate of barytes. The liquid was now mixed with an excess of carbonate of ammonia, boiled for an instant or two, and then filtered, to separate the earth and iron precipitated by the ammonia. The liquid was evaporated to dryness, and the dry mass obtained exposed to a red heat in a silver crucible. The residue was dissolved in water, and exposed in the open air to spontaneous evaporation. The whole gradually shot into regular crystals of sulphate of soda. This salt being exposed to a strong red heat, weighed 50 grains, indicating, according to Berthollet's late analysis, 23.5 grains of pure soda. It deserves to be mentioned, that during this process the silver crucible was acted on, and a small portion of it was afterwards found among the sulphate of soda.

“ This portion was separated before the sulphate of soda was weighed.

“ The preceding analysis gives us the constituents of soda-lite as follows :—

Silica	38.52
Alumina	27.48
Lime	2.70
Oxide of iron	1.00
Soda	23.50
Muriatic acid	3.00
Volatile matter	2.10
Loss	1.70
	<hr/>
	100.00

“ Mr. Allan sent a specimen of this mineral to Mr. Ekeberg, who analyzed it in the course of last summer. The constituents which he obtained, as he states them in a letter to Mr. Allan, are as follows :—

Silica	36.
Alumina	32.
Soda	25.
Muriatic acid	6.75
Oxide of iron	0.25
	<hr/>
	100.00

“ This result does not differ much from mine. The quantity of muriatic acid is much greater than mine. The lime and the volatile matter which I obtained escaped his notice altogether. If we were to add them to the alumina it would make the two analyses almost the same. No mineral has hitherto been found containing nearly so much soda as this. Hence the reason of the name by which I have distinguished it.”

Section III. OF THE COMBINATIONS OF LITHIUM.

LITHIUM has been found in a very few minerals only. It is contained in largest quantity in the *triphane* or *spodumene*, which consists of

Silica	66.
Alumina	25.
Lithia	9.
A trace of oxide of iron.	<hr/>
	100.

Triphane has been found in Sweden, in the Tyrol, and in Ireland. Its colour is greyish-green; it is translucent, hard, and brittle: sp. gr. 3.2. It occurs massive, and its structure is lamellar, and fibrous.

Petalite, according to the corrected analysis of M. Arfwedson, consists of

Silica	77.
Alumina	17.
Lithia	6.
						<hr/> 100.

Petalite has hitherto been found in Sweden only; its colours are reddish, greenish, or grayish white. It is translucent, lamellar, and hard: sp. gr. 2.6.

These minerals may be analyzed by the following process:—

Reduce 50 grains, in an agate or steel mortar, to a very fine and impalpable powder, and mix it with thrice its weight of precipitated carbonate of baryta; give the mixture a red heat for an hour in a silver crucible, wash out the contents, add a small excess of muriatic acid, and evaporate to dryness; boil the dry residue in 12 parts of water, and filter when cold; the silica will remain on the filter, and may be washed, ignited, and weighed.

The filtered liquor (*a*) holds the muriates of baryta, alumina, iron, and lithia: add solution of sulphate of ammonia as long as it occasions a precipitate, which separate, and wash, adding the washings to the filtered liquor (*b*); the baryta is thus removed in the state of sulphate.

To the filtered solution (*b*) add carbonate of ammonia, to throw down the alumina and iron, which collect, and wash, adding the washings to the third filtered liquor (*c*). The mixed precipitate of alumina and oxide of iron may be digested in potassa, which takes up the former, leaving the oxide of iron to be collected, washed, ignited, and weighed.

Evaporate the filtered solution (*c*) to dryness, and ignite the residuum in a silver crucible; the ammoniacal salts are driven off, and pure chloride of lithium remains, from which the lithia may be obtained by carbonate of silver, as above stated. Berzelius gives the following process for the discovery of lithia in minerals. Heat a small fragment before the blow-

pipe with excess of soda upon a piece of leaf platinum; the lithia is liberated when the substance fuses, and the platinum surrounding the fused alkali becomes of a dark colour.

Section IV. OF THE COMBINATIONS OF CALCIUM.

For the manufacture of mortar, lime should be entirely free from carbonic acid, the presence of which is ascertained by the effervescence occasioned on adding muriatic acid to a portion of the lime slaked in; and diffused through, water.

To ascertain the quantity of carbonic acid in carbonate of lime, or other carbonate, proceed as follows:—Provide a thin light phial, capable of holding about six ounces, with a mouth of half an inch diameter; pour into this phial one ounce of nitric acid, diluted with its bulk of water, taking care not to soil the neck; stop it with a plug of cotton wool, and counterbalance the whole in the scale of a delicate beam. Having now weighed off 100 grains of the carbonate, place a hundred grain weight in the scale with the counterpoise, and carefully introduce the carbonate, broken into pieces, into the acid; stop the phial loosely with the wool, and suffer the carbonate to dissolve; during this operation the carbonic acid will escape through the cotton plug, which prevents any particles of liquid being thrown out during the effervescence, and the counterpoise scale will preponderate in consequence of the loss of weight sustained by the carbonate from the evolution of its carbonic acid. When the solution is complete, open the phial, and blow through it by a glass tube, so as to displace the included atmosphere; replace the plug, and bring the balance to an equipoise by adding weights to the scale containing the phial, which weights will show the quantity of carbonic acid lost by 100 grains of the carbonate. If pure carbonate of lime be employed, the loss will amount to 44 grains.

We will suppose, however, that a limestone has been operated on not perfectly soluble in the acid, and containing magnesia and alumina; the other steps of the analysis are as follow:

The insoluble portion must be separated by decantation, collected upon a filter, washed and dried, the washings being added to the original solution. It is probably silica.

The solution we will suppose to contain lime, magnesia, and alumina; to separate these earths, add carbonate of potassa in very slight excess; boil the mixture, collect and wash the precipitate, which will consist of the carbonates of lime and magnesia, and alumina; digest it, while moist, in solution of pure potassa, which dissolves out the alumina; pour the whole upon a filter, washing the insoluble portion, and add to the filtered liquid (which is the alkaline solution of alumina) a slight excess of oxalic acid; collect, wash, and dry the precipitate, at a red heat, in a platinum crucible, and weigh it; it is pure alumina. The separation of the magnesia and lime may be effected by the processes above described.

The analysis of *sulphate of lime* may be effected by an alkaline carbonate as follows:

Reduce 50 grains of the sulphate to a very fine powder, and boil it for half an hour in a Florence flask, with 100 grains of carbonate of soda, dissolved in four ounces of water; the lime will thus be converted into carbonate, which, collected upon a filter, washed, and dried at 500° , will give, either by inference or analysis, the proportion of lime.

The filtered solution will contain the sulphuric acid of the sulphate, the quantity of which may be learned by adding muriate of baryta, and digesting the precipitate in dilute muriatic acid, to remove any carbonate of baryta; the insoluble residuum, washed and duly dried, gives the equivalent of the sulphuric acid.

The proportion of water of crystallization in the sulphates of lime, may be arrived at by exposing 100 parts in fine powder, to a red heat; the loss indicates the quantity of water *per cent*.

The analysis of a mixture of carbonate and phosphate of lime may be performed in the following manner:

Dissolve in dilute nitric acid, and add pure ammonia to the solution, which causes a precipitate of phosphate of lime, equivalent, when dry, to that existing in the original mixture.

Having separated the phosphate by filtration, add carbonate of ammonia, which throws down carbonate of lime; collect, wash, and dry it.

It is generally supposed that the quantity of acid and of base in phosphate of lime may be learned by the following process:—Dissolve 50 grains of the phosphate in as small a quantity as will take it up of nitric acid, diluted with its bulk of water: to this solution add oxalate of ammonia, which will cause a precipitate of oxalate of lime, which may be separated, ignited to whiteness, and weighed; it gives the pure lime. Phosphate of ammonia is retained in the solution, which, evaporated to dryness, and heated red hot in a platinum crucible, gives pure phosphoric acid: or, the solution may be decomposed by the addition of nitrate of lead, which gives an insoluble phosphate of lead, of which 100 parts indicate about 20 of phosphoric acid. But phosphate of lime is only partially decomposed by oxalate of ammonia and nitrate of lead. Phosphate of lime boiled with carbonate of potassa, gives rise to the production of carbonate of lime and phosphate of potassa; but the decomposition is not entire.

No accurate analysis has hitherto been made of the varieties of *fluor spar*; and we are ignorant of the nature of the colouring principle of the blue variety; it fades by exposure to light, and is destroyed by a heat below redness.

When 100 grains of pure and colourless fluor spar, previously heated red hot, are boiled to dryness in a silver crucible, with 200 of sulphuric acid, and the dry mass exposed to a red heat, 190 parts of dry sulphate of lime are obtained, equivalent to about 78 of lime. If we regard fluor spar as a fluoride of calcium, the 78 of lime being equivalent to 56 of calcium, would give the composition of that substance

56 calcium

44 fluorine.

The number 28, as the equivalent of lime, is that given by Dr. Wollaston in his valuable observations upon the synoptic scale of chemical equivalents, and regarding it as containing one-third the quantity of oxygen existing in the proportion of sulphuric acid that combines with it to form sulphate of lime, the number 20 may be regarded as the correct equivalent of calcium.

Section V. OF THE COMPOUNDS OF BARIUM.

By dissolving 100 grains of *native carbonate of baryta*, previously dried at a red heat, in muriatic acid, with the precautions above-directed, they will be found to lose 22 grains of carbonic acid; hence the carbonate consists of

Baryta	78
Carbonic acid	22
						<hr/> 100

If we now precipitate the muriatic solution by carbonate of ammonia, collect the precipitate and dry it at a dull red heat, we shall find it to weigh 100 grains, showing that the composition of the native and artificial carbonate is similar.

If we precipitate the muriatic solution by dilute sulphuric acid, the precipitate of sulphate of baryta properly dried weighs 118 grains; hence the artificial sulphate is composed of

Baryta	.	.	.	78	=	66
Sulphuric acid	.	.	.	40	=	34
				<hr/> 118		<hr/> 100

100 grains of carbonate of baryta dissolved in nitric acid, evaporated to dryness, and exposed for half an hour to a red heat, gave 78 grains of pure baryta.

These results, which closely agree with the original analyses of Dr. Withering (*Phil. Trans.* 1784), and of Klaproth (*Analytical Essays*, i.), furnish the number 78 as the representative of baryta. Deducting from this number one-third of the weight of the oxygen in sulphuric acid = 8, gives 70 as the theoretical equivalent of barium.

The only compound mineral hitherto discovered containing baryta, is the *harmotome* or *cross-stone*; in that from Andreasberg, Klaproth found

Silica	49
Alumina	16
Baryta	18
Water	15
						<hr/> 98

The analysis of this compound may be made by fusing it in fine powder with three parts of potassa, solution in muriatic acid, and evaporation to dryness; pour water upon the dry mass, which leaves silica; to the solution add sulphate of ammonia, which throws down the baryta in the state of sulphate; separate it by a filter, evaporate the filtered liquor to dryness, and give it a red heat; re-dissolve the dry residue in water, and add ammonia, which throws down alumina.

Section VI. OF THE COMPOUNDS OF STRONTIUM.

THE analysis of the *sulphate* and *carbonate of strontia* may be performed in the same way as that of the corresponding compounds of baryta.

Strontia has been found by Mr. Stromeyer in some varieties of *arragonite*, and where it exists in small proportion with carbonate of lime, its presence is not easily detected.

I dissolved 5 grains of carbonate of strontia and 95 of carbonate of lime in nitric acid; added sulphate of ammonia to the solution, collected the precipitate, and washed it with repeated affusions of hot water; when dry, it weighed 6.3 grains, and was sulphate of strontia. Ignited with half its weight of charcoal, and digested in dilute muriatic acid, it afforded a solution of muriate of strontia, the properties of which are easily distinguished from those of muriate of baryta.

The number 44, as the equivalent of strontium, and 52 as that of strontia, are deduced from the analyses of the sulphate and of the carbonate. They are the numbers furnished by Stromeyer's analyses.

Section VII. OF THE COMPOUNDS OF MAGNESIUM.

WHEN 100 parts of pure *crystallized sulphate of magnesia* are exposed to a red heat for one hour, they lose, upon the average of several experiments, *52 per cent.* of water of crystallization; the residue is perfectly soluble in water, and consequently no acid has been expelled: if, to its aqueous solution, we add muriate of baryta, and collect and dry the precipitate, it will be found to indicate 32.5 of sulphuric acid; hence the composition of the crystallized salt.

Besides the adulteration of sulphate of magnesia with sulphate of soda, already adverted to, the salt, as it occurs in commerce, is often deliquescent from the presence of muriate of lime, and muriate of magnesia: the presence of muriatic acid is shown by sulphate of silver; and of lime, by oxalate of ammonia, or by bicarbonate of ammonia, which does not throw down magnesia. Sea salt is not unfrequently found in considerable proportion, mixed with sulphate of magnesia, and which is not thus rendered deliquescent: it is recognised by its salt taste, by the action of sulphate of silver, and by pouring sulphuric acid upon it, which disengages muriatic vapours, easily known by the dense white fumes occasioned by holding a stopper moistened with liquid ammonia above the salt.

I have sometimes found amongst Epsom salt a very considerable proportion of the triple sulphate of magnesia and potassa. It is known by its sparing solubility, and by the rhomboidal form of its crystals: it occasions a grittiness in the mouth, and is less bitter than sulphate of magnesia.

Carbonate of Magnesia, when precipitated in the usual way, and dried at 212° , always retains a portion of water, which it loses by exposure to a red heat along with its carbonic acid. Lime is a very common impurity both in carbonate and calcined magnesia, being frequently derived from sulphate of lime contained in the water used for edulcorating the precipitated carbonate. To the calcined magnesia it gives an acrid alkaline taste. The presence of lime is detected by dissolving the magnesia or its carbonate in mu-

riatic acid, and adding solution of bicarbonate of ammonia, which throws down carbonate of lime, but does not affect a pure magnesian solution. When carbonate of lime is fraudulently added to carbonate of magnesia, as is sometimes the case, it is detected in the same way.

The separation of lime and magnesia, when present in the same solution, has already been adverted to. (Vol. i. p. 484.)

The analysis of mineral substances containing magnesia may in some cases be performed in the humid way; but where the stone resists the action of acids, fusion with alkaline bodies must be resorted to. As instances of these analyses, the reader is referred to Klaproth's examination of the *chrysolite* and of *olivine*, in the seventh and eighth sections of the first volume of his *Analytical Essays*. The following instances may serve further to illustrate the separation of magnesia in cases of complex chemical analysis.

A. 100 parts of red and green-veined primitive *serpentine* were exposed to a dull red heat for half an hour, and were found to have lost 6 grains.

B. The remaining 94 grains, reduced to fine powder, were digested in muriatic acid diluted with two parts of water, and when it no longer acted upon the residue it was decanted off, the residue washed, and the washings added to the muriatic solution. The undissolved portion, when dried at a red heat, weighed 38 grains, and had the properties of pure silica.

C. The muriatic solution supersaturated with liquid bicarbonate of ammonia afforded a brown precipitate, which was collected, washed, and dried; it weighed 25.5 grains, and was found to contain no alumina; it dissolved entirely and with effervescence in muriatic acid, and this solution was evaporated to dryness, the dry residue dissolved in water, and this solution precipitated by oxalate of ammonia, yielded oxalate of lime, which, collected and ignited to whiteness, afforded 13 grains of pure lime: the liquor, from which this oxalic precipitate had been obtained, left, after evaporation and ignition, 2.5 grains of red oxide of iron, equivalent to about 2.2 grains of the black oxide, in which state the metal probably exists in *serpentine*.

D. The solution, from which the precipitate noticed in the last paragraph had been separated, was next evaporated to

dryness, and the residue exposed to a red heat in a platinum capsule, till it ceased to lose weight; in this way 40 grains of magnesia, slightly tinged by an inappreciable portion of oxide of iron, were obtained.

E. It accordingly appears from the above analysis, that 100 parts of precious serpentine contain

	Grains.
A. Water	6.
B. Silica	38.
C. Lime	13.
Oxide of iron	2.2
D. Magnesia	40.
Loss8
	<hr/>
	100

Another specimen of serpentine, from the Lizard, lost 7 grains of water by heat; (*a*) digested in muriatic acid, it gave 43.5 grains of silica; (*b*) the muriatic solution was saturated with carbonate of ammonia, filtered and evaporated to dryness; the dry residue, after having been heated red-hot, gave 30.7 grains of magnesia; (*c*) upon the filter there remained a precipitate of a brown colour, which was dissolved in muriatic acid; pure ammonia added to this solution, gave a precipitate weighing 13 grains, and resolved by potassa into 10 grains of peroxide of iron = 9 protoxide, and 3 grains of alumina. (*d*) The muriatic solution, after the separation of the precipitate by pure ammonia, gave, on adding carbonate of ammonia, 5.3 grains of carbonate of lime = 3 grains of lime. This specimen, therefore, of serpentine, was composed of

Water	7.0
<i>a</i> Silica	43.5
<i>b</i> Magnesia	30.7
<i>c</i> Oxide of iron	9.0
<i>c</i> Alumina	3.0
<i>d</i> Lime	3.0
	<hr/>
	96.2

There are some magnesian stones, such for instance as the chrysolite and the olivin, which are so hard as to resist to a considerable extent, even when pulverized, the action of muriatic acid: in conducting their analysis, they should be previously fused with potassa. If alumina be present, it may be thrown down from the muriatic solution together with the lime, by carbonate of ammonia, and afterwards separated by the action of solution of potassa.

Section VIII. OF THE COMPOUNDS OF MANGANESE.

THE *gray radiated ore of manganese*, when digested in fine powder in muriatic acid, is entirely dissolved, with the exception of a small but variable portion of silica, not exceeding 3 to 4 *per cent.*

The solution contains manganese with a small quantity of iron, which may be very conveniently separated by the action of ammonia, as recommended by Mr. Hatchett, and which, if added so as to saturate the muriatic acid, throws down the iron, but not the manganese.

The oxide of iron may be separated by filtration, and ignited with a little wax, which, when burned off, leaves protoxide of iron.

The filtered solution may be evaporated to dryness, and the residue moistened with nitric acid, and again evaporated and ignited: it is deutoxide of manganese.

Manganese, as has been shown by Mr. Faraday (*Quarterly Journal*, vi. 357), readily forms triple salts with ammonia, and as these salts are not affected by the fixed alkalis, they are often conveniently formed in those analytical operations, the object of which is to separate manganese from other metals. Upon this principle he proposes the following method of decomposing a mixed salt of manganese and iron. To a mixed solution of iron and manganese, add solution of muriate, sulphate, or nitrate of ammonia, and then pour in pure potassa; the iron will be precipitated immediately, but the manganese will remain in solution as a triple salt, unaffected by the free alkalis.

In this method of analysis the muriate or sulphate of ammonia is preferable to the nitrate, because the latter may in some cases produce peroxide of manganese, which would be precipitated; the quantity of ammoniacal salt added should, for the sake of security, be about twice that of the salt of manganese in solution, and as protoxide of iron is soluble in ammonia, any excess of that alkali should be driven off by heat, to ensure a total precipitation.

The black oxide of manganese, as it occurs in commerce, is

very often adulterated with chalk, which is detected by digesting a given weight of it in nitric acid diluted with 10 parts of water; if the oxide be pure, the acid thus diluted is without any immediate action; if it contain carbonate of lime, an instant effervescence ensues, and a nitrate of lime is formed, which may afterwards be decomposed by carbonate of potassa, and the weight of the precipitate when dry shows the quantity of the carbonate present.

Section IX. OF THE COMPOUNDS OF IRON.

THE assay of those native oxides of iron which are the sources of the pure metal, may be performed as follows: reduce the ore to a very fine powder, and mix it with its weight of powdered green-bottle glass, half its weight of chalk, and one-fourth of charcoal; expose this mixture to the full heat of a wind furnace for about an hour; suffer the crucible to cool slowly, and on breaking it, a button of metal will be found at the bottom, covered by the other materials, fused into a dense slag. If the ore contain any mixed pyrites, it should be previously roasted in a muffle or reverberatory furnace.

The analysis of the *magnetic*, *specular*, and *hæmatitic oxides of iron* is sufficiently simple, and may be accomplished in the following manner:—

a. Reduce the ore to a very fine powder, and mix it in a silver crucible with three or four parts of liquid potassa; evaporate to dryness, and expose the residue for about fifteen minutes to a dull red heat; when cold, reduce it to powder and dissolve in muriatic acid, evaporate nearly to dryness, and boil the residue in water; the silica remains, and may be separated by filtration. (*b*) The filtered solution of permuriate of iron may now be evaporated to a small bulk, and decomposed by potassa, which added in excess and boiled upon the precipitate, leaves peroxide of iron, and which, having been washed, dried, and ignited with wax, is restored to the state of protoxide. (*c*) The filtered alkaline liquor now retains alumina, if any

were present, which may be thrown down by muriate of ammonia, washed, and dried.

It sometimes happens that manganese is present in the muriatic solution *b*, and that it is thrown down with the oxide of iron: if this be the case, redissolve the precipitate, after its treatment by alkali, in muriatic acid, and *neutralize* by ammonia, which throws down the oxide of iron, but retains that of manganese.

Chloride of Iron was analyzed as follows: (*a*) 100 grains were dissolved in water; and the solution decomposed by ammonia afforded a precipitate, which when washed, dried, and ignited with wax, was black oxide of iron, weighing 56.5 grains, and equivalent to 44 grains of metallic iron. (*b*) The filtered solution from which the oxide of iron had been separated was neutralized by nitric acid; nitrate of silver was then added, and the precipitated chloride of silver being collected and ignited weighed 227 grains, which is equivalent to 56 grains of chlorine; hence it appears that protochloride of iron consists of

44 iron
56 chlorine
100

By a similar process, the perchloride of iron may also be analyzed.

The native sulphuret of iron, or *magnetic pyrites*, was examined by Mr. Hatchett in the following way (*Phil. Trans.* 1804):

A. 100 grains, reduced to a fine powder, were digested with two ounces of muriatic acid, in a glass matrass placed in a sand-bath. A pale yellowish green solution was formed. The residuum was then again digested with two parts of muriatic acid, mixed with one of nitric acid; and a quantity of pure sulphur was obtained, which, being dried, weighed 14 grains.

B. The acid in which the residuum had been digested, was added to the first muriatic solution; some nitric acid was also poured in, to promote the oxidizement of the iron, and thereby to facilitate the precipitation of it by ammonia, which was added after the liquor had been boiled for a considerable time. The precipitate thus obtained was boiled with lixivium of

potash; it was thenedulcorated, dried, made red-hot with wax in a covered porcelain crucible, was completely taken up by a magnet, and, being weighed, amounted to 80 grains.

c. The lixivium of potash was examined by muriate of ammonia, but no alumina was obtained.

d. To the filtrated liquor from which the iron had been precipitated by ammonia, muriate of barytes was added, until it ceased to produce any precipitate; this was then digested with some very dilute muriatic acid, was collected, washed, and, after exposure to a low red heat for a few minutes in a crucible of platina, weighed 155 grains. If, therefore, the quantity of sulphur, converted into sulphuric acid by the preceding operations, and precipitated by barytes, be calculated according to the accurate experiments of Mr. Chenevix, these 155 grains of sulphate of barytes will denote nearly 22.50 of sulphur; so that, with the addition of the 14 grains previously obtained in substance, the total quantity will amount to 36.50.

e. Moreover, from what has been stated, it appears that the iron which was obtained in the form of black oxide, weighed 80 grains; and, by adding these 80 grains to the 36.50 of sulphur, an increase of weight is found = 16.50. This was evidently owing to the oxidizement of the iron, which, in the magnetical pyrites, exists quite, or very nearly in the metallic state, but, by the operations of the analysis, had received this addition. The real quantity of iron must, on this account, be estimated at 63.50.

100 grains, therefore, of the magnetical pyrites, yielded,

$$\begin{array}{rcl} \text{Sulphur} \left\{ \begin{array}{l} \text{A. } 14. \\ \text{D. } 22.50 \end{array} \right\} & & 36.50 \text{ grains.} \\ \text{Iron} \quad . \quad \text{E.} & = & \frac{63.50}{100} \text{,,} \end{array}$$

The other varieties of pyrites were analyzed precisely in the same way.

100 parts of *crystallized protosulphate of iron* were analyzed as follows: (a) The salt was reduced to powder, and dissolved in a small quantity of nitric acid; the solution was diluted, supersaturated by ammonia, and filtered. In this way the iron was separated in the state of peroxide, amounting to 28.5 grains, equivalent to 25.5 of protoxide of iron. (b) The filtered solution, now perfectly free from iron, but

containing excess of ammonia, was neutralized by nitric acid, and nitrate of baryta was added till it ceased to form a precipitate. The sulphate of baryta thrown down was dried at a red heat and weighed 85 grains, indicating 28.7 of sulphuric acid: hence it appears that 100 grains of crystallized proto-sulphate of iron contain

25.5	protoxide of iron
28.7	sulphuric acid
<hr/>	
54.2	

The loss, amounting to 45.8, is to be attributed to water of crystallization, for 100 grains of the crystals heated to dull redness for a quarter of an hour lose about 45 *per cent.*; hence the salt consists of

54.2	dry sulphate of iron
45.8	water of crystallization
<hr/>	
100.	

The data upon which the composition of oxides of iron is founded, are given in the section on Iron.

The analysis of *phosphate of iron* may be performed as that of phosphate of copper.

The analysis of the different kinds of iron produced by the manufacturer is attended with many difficulties, and has hitherto only been partially performed: on this subject some useful and interesting details will be found in Mr. Daniell's paper "On the mechanical structure of iron, &c." (*Quarterly Journal of Science and Arts*, ii. 278.)

Wootz, or *Indian steel*, was examined in the laboratory of the Royal Institution by Mr. Faraday, as follows, with a view to detect its components, exclusive of carbon and iron.

A piece of wootz, weighing 164.3 grains, was placed in a flask, and acted on by nitro-muriatic acid and heat. It gradually dissolved, and dark-coloured flakes separated from it, which were unalterable in the acid, though boiled with it. When all action had ceased, the solution was poured off from the sediment (*a*) which was repeatedly washed with distilled water; the solution was then examined carefully, but I could find nothing in it but iron. Whilst washing the sediment (*a*) it separated into two parts; a black powder (*b*) sank to the bottom of the water poured upon it, whilst a reddish-brown

substance (c) in flocculi remained suspended; these were parted from each other.

The black powder (b) was fused with potash in a silver capsule, and then dissolved in water; it deposited a brown powder (d), and a clear alkaline solution was obtained. This was saturated with muriatic acid, and evaporated to dryness, and then being redissolved with a little excess of muriatic acid, a very small quantity of white flocculi were left untouched, which were insoluble in acids, and had the characters of *silex*. The solution acted on by subcarbonate of potash gave an abundant precipitate: this was washed, and when heated with a little solution of potash, dissolved in it like *alumine*. Sulphuric acid was then added, and a solution of alum was obtained, a small quantity of *silex* precipitating.

The brown powder (d) deposited by the alkaline solution was treated with nitric acid; a little heat being applied, nearly the whole was dissolved immediately, leaving a little of a black substance. The filtered solution gave a precipitate with muriate of soda, but when ammonia was added to it, the precipitate was redissolved, and a small quantity of iron was thrown down. The solution contained, therefore, *silver*, from the capsule in which the fusion had been made, and *iron* derived from the wootz. The black substance left by the nitric acid, was nearly all dissolved by nitro-muriatic acid, iron being taken into solution, and a little of the substance (b) remaining.

The reddish-brown substance (c) was not affected by nitric acid, but, on adding solution of pure potash to it, a clear deep brown solution was obtained, and a blackish-brown sediment (e) remained. When the alkali of the solution was neutralized by muriatic acid, flocculi were precipitated, and the solution became colourless: these flocculi collected together and dried, proved to be combustible, and appeared to be merely modified tannin. The brown sediment (e) being then examined by muriatic acid, gave oxide of iron and a little *silex*. (*Quarterly Journal of Science and Arts*, vii. 288.)

Section X. OF THE COMPOUNDS OF ZINC.

THE mode of ascertaining the composition of the oxide of zinc has been explained above; it is only necessary to guard against the impurities of common zinc, which are chiefly iron, lead, and copper; the former is taken up by dilute sulphuric acid, and the two latter metals resist its action, and remain in the form of a black powder. Add to the sulphuric solution excess of ammonia, and apply a gentle heat; the oxide of iron will fall, and upon the addition of carbonate of potassa to the ammoniacal solution and boiling it, the pure oxide of zinc will be thrown down. Cadmium is also found in some of the metallic zinc of commerce.

The *oxide of zinc* of the *Pharmacopæia* is sometimes discoloured by a little iron; adulterated with chalk, or plaster of Paris; or contaminated by lead and arsenic. The presence of iron is shown by its solution in dilute nitric acid, neutralized by ammonia, becoming black with tincture of galls; chalk occasions an effervescence on adding the acid; gypsum is dissolved by boiling water, and detected by oxalate of ammonia and muriate of baryta. White arsenic is found by digesting in acetic acid, and adding solution of sulphuretted hydrogen, which occasions a yellow precipitate, in which arsenic is recognized by its smell when ignited on charcoal; and lead is shown by a black precipitate on adding sulphuretted hydrogen to the acetic solution.

Analysis of Chloride of Zinc.—100 grains of chloride of zinc, obtained by heating the muriate in a glass tube to redness, and weighed while hot, to prevent error from deliquescence, were dissolved in water, and left 4 grains of oxide of zinc; accordingly 104 grains of the same chloride were dissolved, filtered, and decomposed by nitrate of silver, and the precipitate, washed, collected, and dried at a red heat, weighed 203 grains, equal to 50.4 of chlorine. The solution from which the chloride was precipitated contained nitrate of zinc, with a little nitrate of silver; muriate of ammonia was added to throw down the silver, in the state of chloride, which was

separated upon a filter, and the clear liquor, evaporated to dryness, and ignited, afforded 62 grains of oxide of zinc, equivalent to 49.5 grains of metal; hence 100 grains of chloride of zinc gave

$$\begin{array}{r} 50.5 \text{ chlorine} \\ 49.5 \text{ zinc} \\ \hline 100. \end{array}$$

Analysis of Sulphuret of Zinc.—A specimen of yellow blende was analyzed as follows by Dr. Thomson.—*Annals of Philosophy*, iv. 94.

a. 50 grains, in fine powder, were digested for two days in dilute nitric acid; the whole was then thrown upon a filter, and the undissolved residue, washed and dried at 110° , weighed 26 grains.

b. These 26 grains were put upon a watch-glass and heated by a lamp; they burned like sulphur, and left a residue of 22.4 grains; the 3.6 grains of loss were considered as sulphur.

c. The 22.4 grains residue, which had now assumed the appearance of the original blende, were again digested for two days with dilute nitric acid: the second day, as all action was over, and the whole nearly dissolved, the flask was exposed for some hours to a heat of 130° ; the whole was then thrown upon a filter, and the undissolved portion, washed and dried, weighed 0.54 grains.

d. This small residue was burned as before, by which it lost sulphur amounting to 0.16 grains, and 0.38 grains of residue remained.

e. This 0.38 grains had the appearance of small particles of quartz.

f. The two portions of acid liquid, which had been digested on the ore, and which contained the greatest part of it in solution, were mixed together, and almost, but not quite, saturated with carbonate of soda. A considerable excess of caustic ammonia was then poured in. By this alkali the oxide of iron was thrown down in yellowish-red flocks, while the whole of the zinc was held in solution. The oxide of iron being separated by the filter, washed, dried, and heated to redness, weighed 8.5 grains. Now this is equivalent to 5.98 grains of metallic iron.

g. The residual liquor was now boiled in a glass retort down

to half its bulk, in order to drive off the ammonia, and precipitate the oxide of zinc. About one half of that oxide precipitates after a few minutes' boiling, but it requires considerable concentration before the other half falls down. From this circumstance, it is not improbable that ammonia and oxide of zinc unite in two proportions.

The oxide of zinc thus obtained being washed, dried, and heated to redness, weighed 36.4 grains. This is equivalent to 29.32 grains of metallic zinc. It may be proper to mention that the oxide of zinc thus obtained was not quite white, but had a slight tinge of green. I conceived that this might be owing to the presence of copper, but if this metal was actually present, it was in too minute a quantity to be detected by the usual tests.

h. The liquid, thus freed from iron and zinc, was mixed with nitric acid, till it acquired a perceptibly sour taste. This was done to prevent any inaccuracy from the presence of ammonia, if any should still remain in the liquid. A solution of muriate of barytes was then mixed with it. The sulphate of barytes which precipitated, being washed, dried, and heated to redness, weighed 77.616 grains. Now 77.616 grains of sulphate of barytes contain 26.4 grains of sulphuric acid, or 10.56 grains of sulphur. From the preceding analysis it appears that blende is composed of the following ingredients:

Zinc	.	.	29.32	.	.	58.64
Sulphur	.	.	14.32	.	.	28.64
Iron	.	.	5.98	.	.	11.96
Quartz	.	.	0.38	.	.	0.76
			<hr/>			<hr/>
			50.00			100.00

The following process was adopted in the analysis of the crystallized *black blende* of Derbyshire:

a. 100 grains carefully separated from its siliceous matrix, were reduced to a fine powder, and dried at 600°. The loss of weight indicates water.

b. Upon the dried and powdered ore put into a Florence flask, were poured two ounces of nitro-muriatic acid, consisting of two of nitric and one of muriatic acid, in small successive portions, taking care to moderate the effervescence, and when this had subsided, a sulphurous magma floated upon the acid: the flask was placed in a sand heat, and with one addi-

tional ounce of nitro-muriatic acid, was digested until nearly the whole of the sulphur had disappeared, being converted into sulphuric acid. The whole contents of the flask were then poured into a conical glass, to allow a portion of undissolved matter to subside, which was separated by decantation, and proved to be silica, mixed with a little pure sulphur, the quantity of which was determined by burning it off, and ascertaining the loss of weight.

c. The decanted acid liquor was now evaporated considerably, so as to dissipate a portion of its excess of acid, and the residue divided into two equal portions, A and B. To A, considerably diluted with water, was added nitrate of baryta, and the precipitate being collected, washed, and dried at a red heat, was pure sulphate of baryta, and was used as the equivalent of the sulphur in the ore.

d. Carbonate of soda was added to the portion B, which threw down everything, and the precipitate, composed of the carbonate of zinc and peroxide of iron, was digested in liquid ammonia, which took up the carbonate of zinc, leaving the oxide of iron undissolved.

e. The alkaline solution of zinc was decomposed by the addition of muriatic acid in slight excess, and to the acid muriate of potassa a little carbonate of soda was added to ensure the entire separation of the zinc; the zinc precipitate was now washed, dried, and ignited, to reduce it to the state of pure oxide of zinc.

f. This ore contained neither copper nor arsenic, which are sometimes present in it.

Analysis of Calamine.—Mr. Smithson (*Phil. Trans.* 1803) was the first to show that there are two distinct varieties of calamine; the one a true carbonate of zinc, and the other a compound of oxide of zinc and silica.

A specimen of crystallized calamine from Derbyshire afforded in the 100 parts

Silica	0.8
Oxide of iron	1.5
Oxide of zinc	65.0
Carbonic acid	32.7
						<hr/> 100.

The above ore was digested in dilute muriatic acid, in which

it slowly dissolved with effervescence, with the exception of 0.8 grains of silica. The solution was evaporated to dryness, and the dry residue redissolved perfectly in water, leaving no further portion of silica. To this aqueous solution caustic ammonia was added in excess, so as to redissolve the oxide of zinc at first thrown down, and the whole thrown upon a filter, on which there remained 1.5 grains of oxide of iron. The ammoniacal solution was supersaturated by muriatic acid, and carbonate of ammonia was added to throw down the whole of the zinc, which precipitate, being dried and ignited, weighed 65 grains. The filtered solution was evaporated to dryness, and the residue being heated in a platinum capsule, entirely evaporated, and was merely muriate of ammonia. The loss, therefore, of 32.7 parts in the hundred may be regarded as carbonic acid.

A specimen of *electric calamine* in small acicular crystals afforded, by digestion in nitric acid, evaporation to dryness, and re-dissolution in dilute nitric acid, a residue of 38.5 *per cent.* silica, which, being separated by a filter, the filtrated liquor evaporated to dryness, and the dry mass ignited for a quarter of an hour, gave 60 *per cent.* of oxide of zinc. The loss may be regarded as water, for the calamine lost upon ignition 2 *per cent.* in weight.

Assay of Zinc Ores.—To ascertain the value of a sample of zinc ore, two methods may be resorted to. 1. Pick out the impurities and weigh off 1000 grains of the picked ore; give it a dull red heat in a muffle, taking care not to fuse it: mix the roasted ore with half its weight of lamp-black, put it into a small coated glass retort with its neck drawn to a very small aperture, and give it a red heat for one hour; cool it gradually, and the zinc will be found in drops in its neck. 2. Prepare and roast the ore as before, and stratify it in a crucible with its weight of clippings of sheet copper; lute a cover on the crucible, and give it a dull white heat for an hour. When cold, throw the contents into water, by which the brass may be separated from the other matter, and its increase of weight, compared with the original copper, gives the addition of zinc. In this process, however, a portion of zinc is always lost.

Section XI. OF THE COMPOUNDS OF TIN.

THE *Native Oxide of Tin* or *Tin-stone*, in consequence of its mechanical aggregation, is almost insoluble in the acids, but it is rendered soluble by fusion with potassa, as Klaproth first remarked. (*Analytical Essays*, i. 522.) The following is the process given by that excellent analyst; and from the relative proportion of the tin to the oxygen, it appears that the metal exists in this ore in the state of peroxide.

a. 100 grains of tin-stone, from Cornwall, previously ground to a subtile powder, were mixed in a silver vessel with a lixivium containing 600 grains of caustic potash; this mixture was evaporated to dryness, and ignited for half an hour; when the mass, thus obtained, had been softened with boiling water, it left on the filter 11 grains of an undissolved residue.

b. These 11 grains again ignited with six times their weight of caustic potash, and dissolved in boiling water, left now only 1.25 grains of a fine yellowish-grey powder behind.

c. The alkaline solution (*a* and *b*) was saturated with muriatic acid, and oxide of tin was thrown down; this precipitate, redissolved by an additional quantity of muriatic acid, was precipitated afresh by means of carbonate of soda; when lixiviated and dried in a gentle heat, it acquired the form of bright yellowish transparent lumps.

d. This precipitate, being finely powdered, entirely dissolved in muriatic acid, assisted by a gentle heat. Into the colourless solution, previously diluted with from two to three parts of water, I put a stick of zinc, and the tin thus reduced gathered around it in delicate dendritic laminæ of a metallic lustre: these, when collected, washed, dried, and fused under a cover of tallow, in a capsule placed upon charcoal, yielded a button of pure tin, weighing 77 grains.

e. The above-mentioned residue of 1.25 grains, left by the treatment with caustic potash (*b*), afforded with muriatic acid a yellowish solution, from which, by means of a little piece of zinc introduced into it, 0.5 grain of tin was still deposited; Prussian alkali added to the remainder of the solution, pro-

duced a small portion of a light blue precipitate, of which, after subtracting the oxide of tin now combined with it, hardly $\frac{3}{4}$ of a grain remained, to be put to the account of the iron contained in the tin-stone, here examined.

In these experiments (excepting only a slight indication of *silex* amounting to about $\frac{3}{4}$ of a grain), no trace has appeared, either of tungstic oxide, which some mineralogists have supposed to be one of the constituent parts of tin-stone, nor of any other fixed substance. Therefore, what is deficient in the sum, to make up the original weight of the fossil analyzed, must be ascribed to the loss of oxygen; and thus the constituent parts of this ore are, to each other, in the following proportion:—

Tin	77.50
Iron	0.25
Silex	0.75
Oxygen	21.50
						<hr/> 100.

Dr. Davy (*Phil. Trans.* 1812) in his analyses of the *Chlorides of Tin*, separated the metal by the immersion of a plate of zinc: from 67.5 grains of *chloride of tin* he thus procured 42. of metallic tin, whence, inferring the proportion of chlorine from the loss of weight, he concludes that this chloride is composed of

62.22 tin
37.78 chlorine.

In consequence of the volatility of the *perchloride of tin*, it is very difficult to weigh it with perfect accuracy; it was, therefore, poured into a bottle half full of water, the weight of which was previously ascertained, and its quantity inferred by the increase of weight. The water was rendered slightly acid by muriatic acid, and 81.75 grains of the perchloride gave by the immersion of zinc 34 grains of tin: hence 100 of the perchloride may be regarded as consisting of

42.1 tin
57.9 chlorine.

The quantity of chlorine in the chloride of tin cannot be ascertained by nitrate of silver, in consequence of the reduction of a portion of the silver; but having thrown down the

tin by zinc, the dissolved chloride of zinc may be decomposed by nitrate of silver, and thus the quantity of chlorine originally united to the tin may be ascertained.

The following is Klaproth's analysis of the *Cupreous Sulphuret of Tin*, called *tin pyrites*, or *bell-metal ore*, from St. Agnes in Cornwall.

a. 120 grains of finely triturated tin-pyrites were treated with an aqua regia, composed of one ounce of muriatic and half an ounce of nitric acid. Within twenty-four hours the greatest part of the metallic portion was dissolved without heat, while the sulphur floated on the surface; after the mixture had been digested for some time in a sand-heat, I diluted it with water, and filtered; it left 43 grains of sulphur, still mixed with metallic particles; when the sulphur had been gently burnt off on a test, there still remained 13 grains; of which eight were dissolved by nitro-muriatic acid: the remaining part was then ignited with a little wax; upon which the magnet attracted one grain of it. What remained was part of the siliceous matrix, and weighed three grains.

b. The solution of the metallic portion (a) was combined with carbonate of potash; and the dirty-green precipitate thus obtained was re-dissolved in muriatic acid diluted with three parts of water; into this fluid a cylinder of pure metallic tin weighing 217 grains was immersed; the result was, that the portion of copper contained in the solution deposited itself on the cylinder of tin, at the same time that the fluid began to lose its green colour, from the bottom upwards, until, after the complete precipitation of the copper in the reguline state, it became quite colourless.

c. The copper thus obtained weighed 44 grains; by digestion in nitric acid it dissolved, and left one grain of tin behind in the character of a white oxide: thus the portion of pure copper consisted of 43 grains.

d. The cylinder of tin employed to precipitate the copper now weighed 128 grains, so that 89 grains of it had entered into the muriatic solution; from this, by means of a cylinder of zinc, I reproduced the whole of its dissolved tin, which was loosely deposited on the zinc in a tender dendritical form. Upon being assured that all the tin had been precipitated, I collected it carefully, lixiviated it cleanly, and suffered it to

dry; it weighed 130 grains. I made it to melt into grains, having previously mixed it with tallow, under a cover of charcoal-dust, in a small crucible; which done, I separated the powder of the coal by elutriation; among the washed grains of tin, I observed some black particles of iron, which were attracted by the magnet, and weighed one grain; deducting this, there remain 129 grains for the weight of the tin; by subtracting again from these last those 89 grains, which proceeded from the cylinder of tin employed for the precipitation of the copper (*b*), there remained 40 grains for the portion of tin contained in the tin pyrites examined. Hence, including that one grain of tin which had been separated from the solution of the copper (*c*), the portion of pure tin contained in this ore amounts to 41 grains.

The *educts*, or substances, extracted in this process from tin pyrites were consequently

	Grains.
Sulphur	30
Tin	41
Copper	43
Iron	2
Vein-stone or gangue	3
	<hr/>
	119

Which makes, in a hundred parts,

Sulphur	25
Tin	34
Copper	36
Iron	2
	<hr/>
	97

Assay of Tin Ores.—If the ore contain arsenic, it should be powdered, mixed with a little charcoal, and roasted till vapours no longer rise. The residue, mixed with a little pitch and saw-dust, is to be put into a covered crucible, and exposed in a wind-furnace to a bright red heat for half an hour; when cool, break the crucible, and the button of metallic tin will be found at the bottom, which may be cleaned by gentle hammering and a wire brush, and weighed. The richest ores afford about 70 *per cent.* of metal.

Section XII. OF THE COMPOUNDS OF CADMIUM.

WE are as yet too little acquainted with the states of combination in which cadmium exists in its ores, and with the properties of the metal itself, to lay down precise rules for their analysis.

Stromeyer directs the digestion of the mixed oxide of zinc and cadmium in sulphuric acid, and passing through the acidulous solution a current of sulphuretted hydrogen gas: redissolve the precipitate in muriatic acid, evaporate to dryness, dissolve the residue in water, and precipitate by carbonate of ammonia, of which add excess to redissolve oxide of zinc, and of copper, should any be present; carbonate of cadmium remains.

According to Stromeyer, 100 parts of cadmium, when converted into oxide, absorb 14.35 of oxygen, and

$$14.35 : 100 :: 8 : 54$$

So that, upon this datum, the number 54 may be assumed as the equivalent of cadmium; a number, not widely different from that given in the Section on CADMIUM; 62 will thus be the representative of oxide of cadmium.

The following are Stromeyer's analyses of the nitrate, sulphate, and carbonate of cadmium.—Gilbert's *Annalen*, lx.

Nitrate .	{	100	nitric acid
		117.58	oxide of cadmium
Sulphate .	{	100	sulphuric acid
		161.1	oxide of cadmium
Carbonate	{	100	carbonic acid
		292.8	oxide of cadmium

Now, if we deduce the number for the oxide from these data, it will be about 65, which gives 57 as the equivalent of the metal.

Upon the same authority, the chloride, iodide, and sulphuret of cadmium, may each be regarded as composed of one proportional of each of their components, and cadmium may be represented by the number 56.

Section XIII. OF THE COMPOUNDS OF COPPER.

THE method of determining the composition of the *Oxides of Copper* is described in page 60.

Chloride of Copper was thus analyzed by Dr. Davy.—*Phil. Trans.* 1812, p. 172.

a. 80 grains were dissolved in nitro-muriatic acid, and a plate of iron was immersed, upon which copper was precipitated, weighing, when well washed and perfectly dry, 51.2 grains.

b. The same quantity of the chloride, dissolved in nitric acid, and precipitated by nitrate of silver, afforded 117.5 grains of dry chloride of silver.

c. Since chloride of silver contains 24.5 *per cent.* of chlorine, 80 grains of chloride of copper must contain 51.2 grains of copper (a) and 28.8 of chlorine, and 100 will consist of 36 chlorine + 64 copper.

The *Perchloride of Copper* may be analyzed exactly in the same way.

The *Native Black Sulphuret of Copper*, or *Vitreous Copper Ore*, should consist, in theory, of

80 copper
20 sulphur
100

In the following analysis of this ore by Klaproth (*Essays*, i. 542), there is a close approach to these numbers; he probably lost a little sulphur by acidification, which might have been estimated by nitrate of baryta.

a. Upon 200 grains of the ore, coarsely powdered, moderately strong nitric acid was affused, which attacked and dissolved them with frothing and extrication of red vapours. The solution was clear, and the sulphur alone in the ore was left behind, floating in the fluid, in gray loose flocculi, without any other residue, which indicated that no antimony was present. The sulphur collected on the filter was heated in a small crucible to inflammation, and it burned with its peculiar

odour, without any trace of arsenic ; yet leaving a slight portion of oxidised iron and siliceous earth.

b. The solution, which had a pure blue colour, was treated first with muriate and then with sulphate of soda, but these produced no alteration, by which it appears that this ore contains neither silver nor lead.

a. 200 grains of the powdered ore were heated with muriatic acid ; as this alone manifested no action, I added nitric acid by drops, which exerted a strong attack. When the solution of the ore had been accomplished, I separated the fluid from the sulphur floating on the surface, and digested this last with a fresh quantity of muriatic acid, dropping into it some nitric acid ; after which I collected it upon the filter. This sulphur, washed and desiccated, weighed $38\frac{1}{2}$ grains, out of which after its combustion, $1\frac{1}{2}$ grain of siliceous earth remained ; so that the true amount of sulphur was 37 grains.

b. The solution exhibits a grass-green colour. I divided it into two parts. Into one half polished iron was immersed, upon which the copper precipitated. It weighed $78\frac{1}{2}$ grains when washed, and desiccated.

c. In order to ascertain the proportion of iron contained in the ore, I combined the other half of the solution with caustic ammonia added to excess. The iron remained behind, in the form of brown oxide, which, collected on the filter, desiccated and ignited, weighed three grains. But as the iron is contained in the mixture of the ore in the reguline metallic state, these 3 grains give $2\frac{1}{4}$ of metallic iron to be added in the computation.

Therefore, 100 parts of the Siberian vitreous copper ore consist of

Copper, <i>b</i>	78.50
Iron, <i>c</i>	2.25
Sulphur, <i>a</i>	18.50
Silex, <i>a</i>	0.75
						<hr/> 100.

The same method of analysis applies to the other sulphurets of copper or copper pyrites.

The *Ferro-arsenical Sulphuret of Copper* was analyzed as follows, by Mr. R. Phillips. (*Quarterly Journal of Science and Arts*, vii. 100.)

a. Having ascertained that the constituents of this ore are copper, iron, arsenic, and sulphur, I boiled 100 grains of it reduced to powder in nitric acid, until the whole of the metallic matter appeared to be dissolved. 14 grains remained unacted upon by the acid; of these a large portion was evidently pure sulphur; by heat 9 grains were volatilized, and 5 remained, which were merely silica, that had been mechanically mixed with the ore.

b. The nitric solution was decomposed by potash, and being heated with excess of it, peroxide of copper and iron were precipitated together: this mixed precipitate was washed until it ceased to be alkaline, and was then dissolved in nitric acid. To the solution ammonia in excess was added; by this, peroxide of iron was precipitated, and the peroxide of copper held in solution; the former, being separated, washed, and ignited, weighed 13.3 grains, equivalent to 9.26 of iron.

c. The ammoniacal solution of copper was heated, and when the greater part of the ammonia was expelled, potash was added to the solution; and, by continuing the heat, peroxide of copper was precipitated, which, being washed and ignited, weighed 56.6 grains, equivalent to 45.32 of copper.

d. The alkaline solution obtained in *c*, and the water employed to wash the mixed precipitate of oxide of copper and iron, were evaporated together, and then saturated with nitric acid. This solution contained the sulphur and arsenic converted into acids, and combined with potash. Nitrate of barytes being added, sulphate was precipitated, which, being washed and ignited, weighed 126 grains, equal, according to Dr. Wollaston's scale, to 17.14 of sulphur, which, added to 9, before obtained, = 26.14. After this an accident happened to the solution, which prevented the separation of the arsenic acid; therefore,

e. 100 grains of the ore were again treated with nitric acid; with the silica 11 grains of sulphur were obtained, and the nitric solution was decomposed by excess of potash as before, in order to separate the oxide of copper and iron.

f. The alkaline solution being saturated with nitric acid, nitrate of barytes was added to it, as long as precipitation took place. The precipitated sulphate of barytes being washed and ignited, weighed 150 grains, = 20.4 sulphur, which, added to

11, separated without acidifying, = 31.4; the mean quantity of this and the first experiment being 28.74.

g. To the solution from which the sulphuric acid had been separated by nitrate of barytes, nitrate of lead was added as long as arseniate of lead was thrown down; and this, when washed and ignited, weighed 53 grains.

According to Dr. Thomson, 21.25 of arseniate of lead contain 7.5 of arsenic acid, equivalent to 4.75 of arsenic; if then, 21.25 give 4.75; 53 of arseniate of lead will indicate 11.84 of arsenic. It appears, from these experiments, that this ore consists of, nearly,

Silica	5.
Iron	9.26
Copper	45.32
Sulphur	28.74
Arsenic	11.84
							<hr/> 100.16

In performing this analysis, some circumstances occurred which I think worthy of notice. In a preliminary experiment, I endeavoured to separate the copper from the iron by means of ammonia, without previously separating the arsenic acid; this I found impracticable, for it appeared that the arseniate of iron, at first precipitated, was eventually dissolved by the ammonia. In some treatises on chemistry, the arseniate of barytes is described as an insoluble salt; this, as may be deduced from what I have stated, is not the case. I first tried it by pouring a solution of arseniate of potash into one of nitrate of barytes; no precipitation occurred, but, upon standing some days, very delicate feathery crystals of arseniate of barytes were formed, which exhibited the prismatic colours with a splendour equal to that of the noble opal. I have since attempted, but without success, to reproduce the salt having this appearance.

Native Phosphate of Copper was analyzed by Klaproth nearly as follows:—The ore was digested in nitric acid, by which it was entirely dissolved, with the exception of a remnant of silica. The nitric solution was divided into two parts; the phosphoric acid was precipitated from one, in the state of phosphate of lead, by adding acetate of lead; and from the weight of the phosphate of lead, the quantity of phosphoric

acid was calculated. The other half of the solution was acted upon by iron to throw down the copper. He concluded, from these experiments, that the ore contained

68.13	oxide of copper
30.95	phosphoric acid
<hr/>	
99.08	

It does not, however, seem clear whether the native phosphate of copper is a subphosphate of the peroxide, or a neutral phosphate of the protoxide; that is, whether it consists of 75 peroxide + 26 phosphoric acid; or of 67.5 protoxide + 26 phosphoric acid, these compounds requiring further investigation.

Native Carbonates of Copper.—These, as well as the artificial carbonates, have been analyzed by Mr. R. Phillips (*Quarterly Journal of Science and Arts*, iv. 274), and the results are given above (page 71). The following is the process which he employed:—

200 grains of green carbonate of copper heated to redness in a platinum crucible, became perfectly black, and lost 55.6 grains.

I put some nitric acid into a small phial, the stopper of which had been perforated, and a glass tube passed through it, to suffer the escape of the carbonic acid gas; the weight of the phial and acid being taken, I gradually put into it 200 grains of green carbonate of copper in small fragments. When the solution was complete, I found that 37 grains of carbonic acid had been evolved. If, then, from 200 we subtract 55.6, the loss by heat, we have 144.4 as the quantity of peroxide of copper; and if from 55.6 we take 37, the carbonic acid, there remain 18.6 as the proportion of water dissipated by heat. 100 parts of green carbonate of copper consist, therefore, of

Peroxide of copper	.	.	.	72.2
Carbonic acid	.	.	.	18.5
Water	.	.	.	9.3
<hr/>				100.0

On examining the solution, I found it to be pure nitrate of copper.

The following comparative results will show how near, in this instance, experiment agrees with theory, if we regard the

green carbonate of copper, or *malachite*, as consisting of one proportional of peroxide of copper, one of carbonic acid, and one of water ; or as an hydrated subcarbonate.

	Vauquelin.	Phillips.	Theory.
Peroxide of copper . .	70.10	72.2	72.1
Carbonic acid . .	21.25	18.5	19.82
Water . .	8.65	9.3	8.17
	<hr/> 100.00	<hr/> 100.0	<hr/> 100.00

Assay of Copper Ores.—When the ores contain sulphur and arsenic, they are roasted till fumes no longer arise, or reduced to powder and deflagrated with nitre. The residue is mixed with black flux, and exposed for one hour to a bright red heat in a wind-furnace, when a button of copper is formed at the bottom of the crucible, the purity of which may be judged of by its appearance and malleability.

The oxides and carbonates of copper are reduced by simple fusion with black flux, care being taken to raise the heat sufficiently.

Section XIV. OF THE COMBINATIONS OF LEAD.

LEAD constitutes a component part of several complex ores, the analyses of which are described in the sections on antimony and silver.

Galena, or Sulphuret of Lead, may be analyzed by the action of dilute nitric acid, which dissolves the lead and separates the sulphur: the lead may be precipitated by sulphate of soda: 100 grains of the sulphate of lead thus thrown down, after having been dried at a dull red heat, are equivalent to 69 of lead.

Vauquelin analyzed a galena from Cologne, as follows. (*Journal des Mines*, No. 68.) It was heated with very dilute nitric acid; the undissolved residue, consisting of silica and sulphur, was heated to redness, by which the latter was dissipated, and pure silica remained. The nitric solution was decomposed by sulphate of soda, and the sulphate of lead collected, dried, and weighed, to estimate the proportion of metal.

The remaining liquor, being saturated by ammonia, gave a precipitate of oxide of iron ; and lastly, carbonate of ammonia threw down carbonate of lime.

A native *Sulphate of Lead* from Anglesea was thus analyzed by Klaproth : 100 grains, moderately heated, lost 2 of water ; the remainder was fused in a platinum crucible with four parts of carbonate of potassa, which gave a yellow hard mass partly soluble in water ; the insoluble residue when dry was 72 grains of oxide of lead ; it was dissolved in nitric acid, and this solution gave, when decomposed by the immersion of a rod of zinc, 66.8 grains of metallic lead. The alkaline solution from the crucible was saturated with nitric acid, and acetate of baryta added as long as it occasioned a precipitate, which weighed, when quite dry, 73 grains, equal to 25 of sulphuric acid. Hence it appears that this ore contains

66.5 lead	}	= 72 oxide of lead
5.5 oxygen	}	25 sulphuric acid
								<hr/>
								97
Loss, consisting of 1 gr. of oxide of							}	3
iron, and 2 of water	}	<hr/>
								100.

Native Phosphate of Lead was also examined by Klaproth ; it is a distinctive character of this compound, that when fused into a globule before the blowpipe, it assumes, as it cools, a dodecaëdral form. 100 grains of green prismatic phosphate of lead dissolved entirely in nitric acid. Nitrate of silver gave a precipitate of 11 grains of chloride = 2.7 of chlorine. Sulphuric acid added to the warm solution gave 106 of sulphate of lead = 78.4 of oxide of lead : the liquor was then freed from excess of sulphuric acid by nitrate of baryta, and after having been nearly saturated by ammonia, acetate of lead was added ; the phosphate of lead thus precipitated weighed 82 grains = 18.37 of phosphoric acid (more correctly 16.5). In the residuary solution was found a trace of iron.

Native Carbonate of Lead may be thus analyzed. Reduce the ore to powder and introduce 100 grains into a sufficient quantity of nitric acid diluted with about two parts of water ; an effervescence ensues, and the carbonic acid may be estimated

by loss of weight ; it amounted to 16 grains. Filter the nitric solution, and if there be any insoluble residue, it is probably silica ; to the filtered liquor add sulphate of soda, which throws down sulphate of lead, whence the oxide may be deduced ; or immerse a plate of zinc into the nitric solution, which throws down metallic lead : in Klaproth's analysis he thus obtained 77 of metal equivalent to 82.5 of oxide ; whence it appears that the native carbonate contains

16.	carbonic acid
82.5	oxide of lead
<hr/>	
98.5	

These numbers almost exactly agree with the theoretical composition of the carbonate of lead ; the loss amounting to 1.5 may probably be considered as 0.5 carbonic acid, and 1. water.

The *Murio-Carbonate of Lead*, or *Native Muriate of Lead*, as it is generally called, was analyzed as follows, by Mr. Chenevix. (Nicholson's *Journal*, 4to., iv.) 100 grains, dissolved in nitric acid, lost 6 of carbonic acid ; the nitric solution was neutralized by ammonia, and the absence of arsenic, phosphoric, and sulphuric acids proved by tests. Nitrate of silver was then added, which formed a copious precipitate, weighing when dry 48 grains, equivalent, according to Mr. Chenevix, to 8 of muriatic acid : he concludes that the 6 grains of carbonic acid saturated 34 of oxide of lead, and that 8 of muriatic acid saturated 51 of oxide of lead ; and therefore that the ore consists of 59 muriate of lead and 40 carbonate of lead.

Klaproth's analysis agrees almost exactly with that of Mr. Chenevix, and they give the following view of the composition of this ore ; but there is probably some considerable error in the estimate of the muriatic acid, and a new analysis is highly desirable.

Oxide of lead	85.5
Carbonic acid	6.
Muriatic acid	8.5
						<hr/>
						100.0

In the assay of lead ores by fire, a considerable loss is often sustained by the volatilization of the oxide of lead, and by its action upon the crucible, so that the operation is best performed

by humid analysis; the ore may be digested in dilute nitric acid, and to the solution, when filtered, sulphate of soda may be added, which will throw down sulphate of lead; the latter, when washed and dried at a red heat, contains about 68 *per cent.* of the metal.

Section XV. OF THE COMBINATIONS OF ANTIMONY.

THERE are three proper ores of antimony, *Native Antimony*, *Native Oxide of Antimony*, and the *Native Sulphuret*.

Native antimony from Andreasberg was examined as follows by Klaproth (*Essays*, ii. 136). 100 grains in powder were heated with nitric acid, the mixture diluted with water and filtered; muriatic acid, added to the filtered liquor, gave a precipitate of chloride = 1 grain of metallic silver; and the residual liquor gave oxide of iron = .25 gr. of metallic iron. The oxide of antimony upon the filter was perfectly soluble in muriatic acid; a piece of zinc, immersed in this muriatic solution, gave 98 grains of metallic antimony; hence the components are

Antimony	98.
Silver	1.
Iron	0.25
					<hr/> 99.25

The *Native Oxide*, or *White Ore of Antimony*, from Pritzbram in Bohemia, was also analyzed by Klaproth; he found it a perfectly pure oxide, but did not ascertain the relative proportions of its component parts. According to Vauquelin, it contains silica and a little oxide of iron.—Haüy, iv. 274.

The following is the analysis of an *iridescent sulphuret of antimony*, in acicular crystals, from Hungary.

a. 100 grains digested in two parts of nitric acid and one of water afforded a portion of sulphur, which, having been carefully separated from the adhering oxide, burned entirely away. It weighed 17.5 grains.

b. The insoluble oxide, collected and washed, was re-dis-

solved in muriatic acid, and zinc immersed into the solution, by which 74 grains of metallic antimony were thrown down.

c. The nitric solution being evaporated to one-fourth, let fall a portion of white powder, which, treated as *b*, gave 2 grains of antimony.

d. The solution *c* appearing now to be free from antimony, was diluted and divided into two equal portions, A and B. Muriate of baryta added to A, gave a precipitate of sulphate of baryta, weighing 22.5 grains, = about 3 grains of sulphur, or 6 in 100.

e. The portion B tested by muriate of soda gave no indication of silver; supersaturated with ammonia, it let fall 1.5 grains of peroxide of iron, = to about 1 grain of iron.

f. The results of this analysis, therefore, are

Sulphur	.	.	{	a. 20.5 grs.	}	23.5 grs.
				d. 6.		
Antimony	.	.	{	b. 74. grs.	}	76.0
				e. 2.		
Iron	.	.	e.	.	.	2.
						<hr/> 101.5

The small increase of weight I refer to zinc adhering to the antimony.

The *Red Ore of Antimony*, from Braunsdorff in Saxony, was analyzed by Klaproth; he digested it in muriatic acid, and threw down the antimony by water and potassa; the precipitate, after a second solution and precipitation, was re-dissolved in muriatic acid, and decomposed by a piece of polished iron, which caused the separation of 67.5 grains of metallic antimony. The sulphur he estimates at 19.70 *per cent.*, and attributes the loss of weight to oxygen combined with the antimony; he therefore regards the ore as a sulphuretted oxide of antimony, containing

Antimony	67.50
Oxygen	10.80
Sulphur	19.70
							<hr/> 98.

The following is Mr. Hatchett's instructive analysis of *Bournonite*, or the *triple Sulphuret of Lead, Antimony, and Copper*:

A. 200 grains of the ore, reduced to a fine powder, were put

into a glass matrass, and, two ounces of muriatic acid being added, the vessel was placed in a sand-bath. As this acid, even when heated, scarcely produced any effect, some nitric acid was gradually added, by drops, until a moderate effervescence began to appear.

The whole was then digested in a gentle heat, during one hour; and a green-coloured solution was formed whilst a quantity of sulphur floated on the surface, which was collected, and was again digested in another vessel, with half an ounce of muriatic acid,

The sulphur then appeared to be pure, and, being well washed and dried on bibulous paper, weighed 34 grains: it was afterwards burned in a porcelain cup, without leaving any other residuum than a slight dark stain.

B. The green solution, by cooling, had deposited a white saline sediment; but this disappeared upon the application of heat, and the addition of the muriatic acid in which the sulphur had been digested.

The solution was perfectly transparent, and of a yellowish-green: it was made to boil, and in this state was added to three quarts of boiling distilled water, which immediately became like milk; this was poured on a very bibulous filter, so that the liquor passed through before it had time to cool; and the white precipitate thus collected, being well edulcorated with boiling water, and dried on a sand-bath, weighed 63 grains.

c. The washings were added to the filtrated liquor; and the whole was gradually evaporated at different times, between each of which it was suffered to cool, and remain undisturbed during several hours. A quantity of crystallized muriate of lead was thus obtained, until nearly the whole of the liquor was evaporated: to this last portion a few drops of sulphuric acid were added, and the evaporation was carried on to dryness; after which the residuum, being dissolved in boiling distilled water, left a small portion of sulphate of lead.

The crystallized muriate of lead was then dissolved in boiling water; and, being precipitated by sulphate of soda, was added to the former portion, was washed, dried on a sand-bath, and then weighed 120.20 grains.

D. The filtrated liquor was now of a pale bluish-green, which changed to deep blue, upon the addition of ammonia; some ochraceous flocculi were collected, and, when dry, were heated with wax in a porcelain crucible, by which they became completely attractable by the magnet, and weighed 2.40 grains.

E. The clear blue liquor was evaporated nearly to dryness; and, being boiled with strong lixivium of pure potash, until the whole was almost reduced to a dry mass, it was digested in boiling distilled water; and the black oxide of copper, being collected and washed on a filter, was completely dried, and weighed 32 grains.

200 grains of the ore, treated as here stated, afforded,

	Grains.
A. Sulphur	34.
B. Oxide of antimony	63.
c. Sulphate of lead	120.20
D. Iron	2.40
E. Black oxide of copper	32.

But the metals composing this triple sulphuret are evidently in the metallic state; and white oxide of antimony precipitated from muriatic acid by water, is to metallic antimony as 130 to 100; therefore, the 63 grains of the oxide must be estimated at 48.46 grains of the metal.

Again, sulphate of lead is to metallic lead as 141 to 100; therefore, 120.20 grains of the former are = 85.24 grains of the latter. And, lastly, black oxide of copper contains 20 *per cent.* of oxygen; consequently, 32 grains of the black oxide are = 25.60 grains of metallic copper.

The proportions for 200 grains of the ore will, therefore, be,

Sulphur	34.
Antimony	48.46
Lead	85.24
Iron	2.40
Copper	25.60
	<hr/>
	195.70
	<hr/>
Loss	4.30

Section XVI. OF THE COMBINATIONS OF BISMUTH.

THE principal ores of bismuth are, *Native Bismuth*, the *Sulphuret*, the *plumbo-cupriferous Sulphuret*, and the *Native Oxide*. Klaproth's analysis of the bismuthic silver ore will be found in a following section.

The *Sulphuret of Bismuth* has been analyzed by Sage (*Mém. de l'Acad. des Scien.*, 1782, p. 307), but the following more complicated analysis of one of the ores of this metal renders it unnecessary to advert to other details.

The *needle ore* of Siberia, or *Sulphuret of Lead, Copper, and Bismuth*, was examined as follows:—

a. 50 grains, separated as far as possible from its quartzose matrix, were digested in nitric acid diluted with its bulk of water; when all action had ceased, a gentle heat was applied for a few hours, until no further action took place. The whole was then poured upon a filter, and the residue, being washed and dried, weighed 8.8 grains; it was burned, and there remained upon the capsule 2.3 grains of silica; the burned portion, amounting to 6.5 grains, being considered as sulphur. There was also an inappreciable portion of sulphate of lead.

b. The filtered solution being evaporated, let fall crystals of nitrate of lead; the evaporation was carried nearly to dryness, and the residue, put into 8 ounces of water, deposited a quantity of oxide of bismuth, which being collected, washed, and heated, weighed 20 grains. On evaporating the filtered liquor to half its bulk, there was a further deposit of 3 grains of oxide of bismuth. Now, 23 grains of oxide of bismuth may be computed as equal to 20.5 of the metal.

c. The evaporation was now carried nearly to dryness, a portion of excess of acid driven off, and the residue again diluted, by which a very slight turbidness was produced, but no appreciable portion of bismuthic oxide deposited. I therefore poured sulphate of soda into the solution, and the precipitate of sulphate of lead thus formed, weighed, when dry, 18.5 grains, equivalent to about 12.7 of lead.

d. The filtered liquor was now evaporated to dryness, and

the residue dissolved in a small quantity of water; carbonate of soda was added, and the blue precipitate being collected and washed, was digested in ammonia, in which it was totally soluble: the ammonia being driven off, the residue was heated red hot, and had the properties of pure peroxide of copper; it weighed 8 grains, which is nearly equivalent to 6.5 of copper.

These were all the components of this triple sulphuret which I could separate, though, from its odour before the blowpipe, I suspect the existence of a trace of arsenic in it: the following, therefore, are the results of the analysis:—

	Grains.
Sulphur (a)	6.5
Bismuth (b)	20.5
Lead (c)	12.7
Copper (d)	6.5
	<hr/>
	46.2
Silica (a)	2.3
Loss	1.5
	<hr/>
	50.0

From the small quantity of the needle ore in my possession, I could not repeat this analysis, nor could I employ separate portions for the separation of its several components.

Dr. John (*Chemische Untersuchungen*, p. 216), whose analysis is, I believe, the only one previously published, gives the following as the composition of this ore of bismuth:

Bismuth	43.20	21.60
Lead	24.32	12.16
Copper	12.10	6.05
Sulphur	11.58	5.79
Nickel	1.58	0.79
Tellurium?	1.32	0.66
Gold	0.79	0.39
	<hr/>	<hr/>
	94.89	47.44
Loss	5.11	2.56
	<hr/>	<hr/>
	100.00	50.00

It may be observed, that in both these analyses, but especially in the latter, the proportion of sulphur falls short of that required to constitute the respective sulphurets of lead, copper, and bismuth, and that the loss, therefore, may be most plausibly ascribed to sulphur.

The *Native Oxide of Bismuth* consists, according to Lampadius, of

Oxide of bismuth	86.3
Oxide of iron	5.2
Carbonic acid	4.1
Water	3.4

Heat would expel both the water and carbonic acid from this compound: the relative proportion of the latter might be learned by the loss of weight during effervescence. The ore might then be dissolved in the smallest possible quantity of nitric acid, and excess of ammonia would precipitate the peroxide of iron, but retain the bismuth in solution; the oxide of bismuth might then be obtained by evaporation to dryness, and exposure to heat sufficient to decompose the nitrate of ammonia.

Section XVII. OF THE COMBINATIONS OF COBALT.

THE analyses of the chloride and of the sulphate of cobalt are given in the preceding chapter, from which the equivalent of the metal is deduced.

The principal difficulties that occur in examining the combinations of cobalt are, its separation from arsenic, from nickel, and from copper, which may be performed as follows:—

a. 100 grains of an alloy of cobalt, arsenic, nickel, and copper, are digested in nitric acid till perfectly dissolved; the solution is then evaporated to dryness, and a fresh portion of nitric acid distilled off the dry salt, in order to ensure the complete acidification of the arsenic; the residue, consisting of arseniates of cobalt, copper, and nickel, may then be treated by nitrate of lead, which will remove the arsenic acid in the form of insoluble arseniate of lead; but a more convenient method of proceeding is perhaps as follows: boil the arseniates repeatedly in solution of potassa, until that alkali no longer takes up arsenic acid; the oxides of cobalt, nickel, and copper, will thus be obtained nearly, if not quite, free from arsenic acid.

b. To separate the oxides of copper, cobalt, and nickel, dis-

solve them (in the state of hydrates) in dilute nitric acid, and immerse a plate of iron, which will throw down metallic copper, and a mixed nitrate of iron, cobalt, and nickel, will be obtained.

c. To this mixed nitrate add potassa, wash the precipitate, and digest it in ammonia, which will take up the oxides of cobalt and nickel, leaving the peroxide of iron.

d. The ammoniated solution of cobalt and nickel may be treated as directed by Mr. R. Phillips. (*Phil. Magazine*, xvi. 313.) Evaporate it till the excess of ammonia is expelled (which is known by no change of colour being produced by it on turmeric paper), and then add solution of potassa, and dilute considerably; the oxide of nickel instantly falls, but that of cobalt remains some time in solution, and may be obtained by neutralizing the alkaline liquor.

The following is Tassaert's analysis of the *Arsenical Cobalt*, or *White Cobalt Glance* of Tunneberg.

That the reader may better understand the process, it may be premised, that when reguline arsenic is boiled with a *little* nitric acid, it is dissolved and converted into white oxide, all of which is deposited by mere evaporation to a small bulk of liquid; but when *much* nitric acid is used, the arsenic is more or less acidified, becomes thereby much more soluble in water, and then acting as an acid, it readily dissolves cobalt, iron, &c., forming arseniates of those metals, which are decomposable by the fixed alkalis. It may be also added, that oxide of cobalt is soluble in ammonia, but oxide of iron is not; and that the nitrate of iron deposits much of its iron by mere exposure to air, but the nitrate of cobalt remains clear.

A. To estimate the quantity of arsenic separately, M. Tassaert digested 100 parts of the cobalt ore with dilute nitric acid, and in some hours the whole was dissolved, but by cooling, deposited a quantity of white crystalline grains. On evaporation, more of them were deposited, and when all had thus separated, they were collected and dried, and weighed 56 parts, all of which was sublimed by heat except three parts, probably a mixture of arsenic and cobalt. Hence the oxide of arsenic from this ore may be reckoned at about 53 parts, indicating 49 *per cent.* of metallic arsenic in the ore.

B. 300 parts of the ore were then digested with four times

as much nitric acid, which made a rose-coloured solution. By partial evaporation, adding water, and heating, a rose-white precipitate (*a*) fell down, leaving a rose-coloured solution. This solution, boiled with an excess of potash, gave an oxide of cobalt, at first rose-coloured, then passing to green, and, when dried in a red heat, black. It weighed 85 parts.

c. The 85 parts of the last experiment were then examined for iron. When redissolved in nitro-muriatic acid, pure ammonia was added, which gave a precipitate which was all redissolved by an excess of the alkali, except a small portion, which, again treated with nitro-muriatic acid and ammonia, was reduced to 4 parts, and appeared to be oxide of iron.

d. The rose-precipitate of experiment b, which proved to be a mixed arseniate of cobalt and iron, was decomposed by caustic potash in excess, and gave a precipitate weighing 100 parts when dried.

e. The 100 parts of the last experiment were redissolved in nitric acid, the solution evaporated partly, and then diluted with water; a precipitate of oxide of iron, weighing 27 parts, then separated, and a clear solution of cobalt was left.

f. The nitrate of cobalt of the last experiment was decomposed by ammonia, and the precipitate redissolved by an excess of the alkali, except 15 parts of insoluble oxide of iron: the solution was added to the ammoniated cobalt of experiment c.

g. The insoluble precipitates of oxide of iron of c, e, and f, were then mixed and examined: they still gave a blue glass with borax, and therefore contained a certain portion of cobalt. Acetic acid was found a good method of separating them: for this purpose they were redissolved in nitro-muriatic acid, precipitated by just sufficient ammonia, and the precipitate whilst still wet was put into acetic acid. This dissolved the whole at first, but on boiling and evaporating the solution nearly to dryness, most of the iron separated, and by redissolving in water and evaporating nearly to dryness successively four times, nearly all the oxide of iron was rendered insoluble, whilst the cobalt remained in the solution, and this acetited cobalt in proportion as it was freed from iron became more and more of a fine rose colour. This last was then supersaturated with ammonia, and the solution of ammoniated cobalt was

added to the different portions of the same obtained in the former experiments. The whole was then boiled to expel the excess of ammonia, and by adding potash the whole of the pure oxide was precipitated, which, when well washed and dried, weighed 133 parts. This oxide reduced in a crucible lined with charcoal, gave regulus of cobalt in its purest form, of the specific gravity of 8.538, and to all appearance totally free from arsenic and iron.

н. Lastly, to estimate the quantity of sulphur, 100 parts of the ore were separately boiled with 500 of nitric acid, and diluted with water, to separate all the oxide of arsenic that would be deposited spontaneously. All the sulphur being now converted into sulphuric acid by the action of the nitric acid, nitrate of barytes was added, and from the precipitated sulphate of barytes, the quantity of sulphuric acid, and, of course, of sulphur, was estimated according to known proportions.—Aikin's *Dictionary*, i. 307.

Section XVIII. OF THE COMBINATIONS OF URANIUM.

THE *Pechblende* of mineralogists is an oxide of uranium, combined with a little oxide of iron, sulphuret of lead, and silica; probably accidental ingredients, as shown by the following results of Klaproth's analysis of the *pitch ore of uranium*, from Joachimsthal:—

Oxide of uranium	86.5
Oxide of iron	2.5
Sulphuret of lead	6.0
Silica	5.0
					<hr/>
					100.

The following is a general process for the analysis of uranitic ores.

a. Digest in dilute nitric acid, which separates sulphur and silica (if sufficiently dilute without the acidification of the former); burn off the sulphur, and the silica remains.

b. To the nitric solution add sulphate of soda, which separates lead in the state of sulphate.

c. To the remaining solution add liquid potassa in excess, and boil; filter, wash the precipitate, and digest it in pure ammonia, which takes up the copper, and which may be obtained by immersing a plate of zinc in the ammoniacal solution slightly supersaturated with sulphuric acid.

d. Digest the portion of the precipitate c, insoluble in ammonia, in bicarbonate of potassa, which, if used in sufficient quantity, takes up oxide of uranium, leaving oxide of iron.

The *Micaceous Uranite*, from the Gunnis Lake Mine in Cornwall, was analyzed as follows, by Mr. Gregor (*Annals of Philosophy*, v. 281):—

a. 100 grains lost, by exposure to a low red heat, 15.4 grains of water.

b. 100 grains (not previously ignited), repeatedly boiled in excess of nitric acid, left a residue amounting only to 0.1 grain of silica and oxide of iron.

c. Excess of ammonia added to the nitric solution, threw down a yellow precipitate, which, digested in excess of ammonia, gave a blue solution, and left 74.9 grains of oxide of uranium, not quite pure.

d. The ammoniacal solutions were evaporated to dryness, and the residue again digested in ammonia left 0.2 grains of oxide of uranium. The ammoniacal solution again evaporated, and the residue dissolved in nitric acid, gave with potassa a precipitate, which, dried and ignited, was 7.65 grains of oxide of copper.

e. The 74.9 grains of oxide c, digested in dilute sulphuric acid, left a trace of lead. The sulphuric solution, precipitated by excess of ammonia, still showed traces of copper, and by a cylinder of zinc gave 0.5 grains of metallic copper = 0.62 of oxide; so that the 74.9 grains of process c were reduced to 74.28, to which add the 0.2 grains of process d, and it gives the whole amount of oxide of uranium = 74.48. The results of the above analysis are

Oxide of uranium, with a trace of lead	. 74.48
Oxide of copper, d e	. 8.20
Water	. 15.40
	<hr/>
	98.08
Loss	. 1.92
	<hr/>
	100.00

Section XIX. OF THE COMBINATIONS OF TITANIUM.

KLAPROTH and Vauquelin have furnished analyses of the titanitic ores, of which the following examples will suffice.

The *silico-calcareous titanite* from Bavaria was thus analyzed by Klaproth (*Essays*, i. 214).

a. 100 grains in fine powder were ignited for an hour with 400 grains of caustic potassa, and the resulting mass digested in muriatic acid left 12 grains of silica.

b. Carbonate of potassa was added to the muriatic solution, and the precipitate thus obtained, being again digested in muriatic acid, left 23 grains of silica.

c. Caustic ammonia was then added to the preceding solution, and the precipitate dried and ignited gave 33 grains of oxide of titanium.

d. To the remaining fluid, whilst boiling, carbonate of potassa was added, and the precipitate having been duly ignited, gave 33 grains of lime.

The following, then, are the component parts of this mineral :—

	Grains.
Silica, <i>a, b</i>	35
Oxide of titanium, <i>c</i>	33
Lime, <i>d</i>	33
	<hr/> 101

The following is Vauquelin's analysis of the *Menachanite* of Bavaria (*Journal des Mines*, No. 19) :—

a. 100 grains finely pulverized were fused for an hour and a half in a silver crucible, with 400 grains of potassa; the fused mass, digested in water, left 124 grains of red insoluble powder.

b. The 124 grains were boiled with potassa, and the solution, after saturation with muriatic acid, was treated with carbonate of potassa, which threw down 3 grains of oxide of titanium.

c. The residue of the 124 grains was digested with dilute muriatic acid, which left 46 grains of oxide of titanium.

d. The muriatic solution, saturated by ammonia, gave 50 grains of oxide of iron.

e. The alkaline solution *a*, which was of a green colour, was supersaturated by muriatic acid, and evaporated to dryness; the dry residue contained no silica, for it dissolved entirely in water; on the addition of carbonate of potassa, it yielded 2 grains of carbonate of manganese.

Section XX. OF THE COMBINATIONS OF CERIUM.

CERITE was analyzed, with the following results, by Vauquelin (*Annales du Muséum*, v. 412):—

67	oxide of cerium
17	silica
2	oxide of iron
2	lime
12	water and carbonic acid
<hr/>	
100	

The following directions for the analysis of this ore are given by Messrs. Aikin:—

a. Having minutely pulverized the ore, weigh it, then ignite it and weigh it again; the difference may be set down as the amount of water.

b. Digest the calcined ore in repeated portions of nitro-muriatic acid, and when nothing further is taken up, fuse the residue with caustic potash; then dissolve out the mass by muriatic acid, evaporate to dryness, and digest again in very dilute muriatic acid: the insoluble residue is siliceous.

c. Add together the muriatic and nitro-muriatic solutions, and decompose the whole at a boiling heat by saturated carbonate of potash; redissolve the whole in as little muriatic acid as possible, heat the solution to drive off the last remains of carbonic acid, and add perfectly caustic ammonia till there is an evident excess; separate the precipitate, and add to the clear liquor as much muriatic acid as will saturate it, and then throw down from it the lime in the state of carbonate, by means of a mild alkali.

d. The ammoniacal precipitate, consisting of the oxides of cerium and iron, is to be dissolved in muriatic acid, and liquid hydrosulphuret of potash is to be dropped in till the precipitate, which at first will be greenish, becomes white; the clear liquor being separated and treated with carbonate of potash, affords a white precipitate, which is carbonate of cerium.

e. The greenish precipitate is to be dissolved in as little muriatic acid as possible, and the solution being neutralized by an alkali to the point of precipitation, sulphate of soda is to be added, which will throw down a sulphate of cerium; the residual fluid being then decomposed by ammonia, deposits oxide of iron.

f. The sulphate of cerium *e* is now to be boiled with thrice its weight of carbonated soda, by which it will be converted into carbonate, which is to be dissolved in dilute muriatic acid, and again precipitated by carbonate of potash or of soda.

g. The carbonates of cerium (*d* and *f*) are now to be calcined, by which the pure brown oxide of cerium will be obtained. (*Addenda to the Dictionary*, iii. 509.)

Allanite, analyzed by Dr. Thomson (*Edinburgh Phil. Trans.*, vi. 385), was found to contain the following substances:—

Oxide of cerium	33.9
Oxide of iron	25.4
Silica	35.4
Lime	9.2
Alumina	4.1
Water	4.0
					112.0

Section XXI. OF THE COMBINATIONS OF TELLURIUM.

THE following is an outline of the analysis of several compounds of tellurium given by Klaproth, in his *Chemical Examination of the Auriferous Ores of Transylvania* (Essay, ii. 1).

Native Tellurium, from Fatzebay in Transylvania, contains, according to that celebrated analyst,—

92.55	tellurium
7.20	iron
0.25	gold
<hr/>	
100.	

The following method was pursued in the decomposition of this ore:—

a. It was separated as much as possible from its stony matrix and pulverized, was digested in six parts of warm muriatic acid, to which were added, cautiously at intervals, three parts of nitric acid: the compound acid acted violently on the ore, and took up the whole of it except the quartzose matrix.

b. The acid solution being diluted with as much water as it would bear without decomposition, was combined with caustic potassa, upon which a copious precipitate fell down; more alkali was then added, till the whole of the precipitate that was resolvable in this menstruum was taken up. There remained behind a dark-brown residuc, consisting of the oxides of gold and iron.

c. The residuc of *b* was then dissolved in nitro-muriatic acid, to which was afterwards added, drop by drop, nitrate of mercury, prepared in the cold, as long as the precipitate thus formed appeared of a brown colour; this precipitate, consisting of gold and muriate of mercury, was then pretty strongly ignited in a crucible with borax, by which the mercury was driven off, and a button of pure gold remained.

d. To the nitro-muriatic solution *c*, was now added caustic alkali, by which the oxide of iron was thrown down.

e. The alkaline solution *b* was accurately saturated with muriatic acid, and then heated, by which a white heavy powder was obtained; which, after being washed in a mixture of equal parts of alcohol and water, and then gently dried, was pure oxide of tellurium.

The *gray ore of Tellurium*, or *Graphic Gold*, of Offenbanya, contains

60	tellurium
30	gold
10	silver

This ore was treated in the following manner:—

a. The finely pulverized ore was digested in nitro-muriatic acid till nothing more was taken up.

b. The insoluble residue, consisting of quartz and muriate of silver, was fused with five times its weight of carbonated soda, by which the silver was obtained in the metallic state.

c. The nitro-muriatic solution being concentrated by evaporation, was largely diluted by alcohol, upon which the oxide of tellurium precipitated; and this being redissolved in muriatic acid, was obtained in black metallic flocculi, by means of a bar of polished iron.

d. The nitro-muriatic solution *c*, after separation of the tellurium, contained only gold, which was procured by the addition of a solution of green sulphate of iron.

The *yellow ore of Tellurium*, from Nagayag, is composed, according to Klaproth, of

44.75	tellurium
26.75	gold
19.50	lead
8.50	silver
0.50	sulphur
<hr/>	
100.	

He performed the analysis of this ore nearly as follows:—

a. 400 grains of the pulverized ore were digested with nitric acid, till every thing soluble in this fluid had been taken up.

b. The nitrous solution was combined with muriatic acid, as long as any precipitation took place; by this there was obtained 51 grains of a white powder, of which 43 grains were again resolvable in boiling water. The insoluble portion, amounting to 8 grains, was muriated silver.

c. The solution, containing the 43 grains above-mentioned, was concentrated by gradual evaporation, and afforded delicate needle-form-crystals of muriated lead.

d. The residue of *a*, insoluble in nitric acid, was then treated with nitro-muriatic acid, as long as any thing was taken up; the solution was mixed with the nitro-muriatic solution *b*, and reduced by evaporation till it ceased to deposit muriate of lead: 11 grains were thus obtained.

e. To the concentrated solution *d*, was added caustic potash in excess, which threw down a copious blackish-brown precipitate; this being separated, the alkaline liquor was saturated with muriatic acid, and the white precipitate thus obtained, being again dissolved in muriatic acid, and then precipitated

by means of a stick of zinc, afforded 85 grains of metallic tellurium.

f. The blackish-brown precipitate of *e* was dissolved in nitro-muriatic acid, and the liquor was nearly saturated with caustic potash; nitrated mercury was then added, till the precipitate began to be white; this precipitate being separated by the filter, and washed, the filter, with its contents, was ignited in a crucible, and a little nitre being added, the fire was increased, and a button of pure gold was thus obtained, weighing 50.75 grains.

g. The remainder of the nitro-muriatic solution *f* was saturated with carbonated potash, and a precipitate was obtained, consisting of oxide of manganese, mixed with carbonated lime, and a little alumine and oxide of iron.

h. The insoluble residue of *d*, weighing 120.5 grains, and consisting chiefly of quartz, was gently heated, by which it lost about 1 grain, which was sulphur; being then mixed with four times its weight of carbonated potash, and fused, there was obtained a button of silver, weighing 10.125 grains.

The *black ore of Tellurium*, also from Nagayag, according to the same analyst, consists of

54.0	lead
39.2	tellurium
9.0	gold
0.5	silver
1.3	copper
3.0	sulphur
<hr/>	
100.0	

This ore was analyzed in the following manner:—

a. 1000 grains of the pulverized ore were digested with 10 ounces of muriatic acid, to which was added, by degrees, a little nitric acid: this being poured off, 5 ounces more of muriatic acid were added, by which every thing soluble in this menstruum was taken up; to the filtered solution boiling water was added, to redissolve the muriate of lead which had begun to be deposited.

b. Of the insoluble residue a part had cohered into a mass, and was for the most part sulphur, weighing 17.5 grains; being gently ignited, it left behind 3.5 grains of a blackish matter, which was dissolved in muriatic acid, and added to the fore-

going solution. Hence the sulphur of the ore amounted to 14 grains.

c. The remainder of the insoluble residue was for the most part quartz, and weighed 440.5 grains. Being melted with four times its weight of carbonated potash, there appeared, on breaking the mass, a few globules of silver, amounting to about 2.5 grains, equivalent to 3.5 grains of muriated silver; so that the quartzose matrix was equal to 437 grains.

d. The solution *a* being concentrated by evaporation, crystals of muriated lead were deposited, to the amount of 330 grains, equivalent to 248 of metallic lead.

e. Having thus separated the lead, the remainder of the solution was largely diluted with alcohol, by which a white oxide of tellurium was thrown down; this oxide being redissolved by muriatic acid, and again precipitated by caustic soda, afforded 178 grains of oxide, equivalent to 148 grains of reguline tellurium.

f. The alcoholic solution was next distilled, by which the alcohol was separated: the residual fluid being diluted with water, was treated with nitrate of mercury, in the way already described, by which a button of gold, weighing 41.5 grains, was obtained.

g. The residual fluid of *f* was saturated with carbonated soda, and boiled, by which a bluish-grey precipitate was obtained: by digestion in muriatic acid it dissolved, and oxymuriatic acid gas was produced; the muriatic solution being then supersaturated with carbonated ammonia, there was deposited carbonated manganese, mixed with iron, to the amount of 92 grains.

h. The ammoniacal solution was of a blue colour, upon which it was supersaturated with sulphuric acid, and a plate of iron being immersed in the fluid, there were deposited 6 grains of copper.

The above abridged account of Klaproth's analyses of the ores of tellurium is extracted from Messrs. AIKIN's *Dictionary*, and contains a variety of instructive details to the student in analytical chemistry.

The following analysis of a supposed ore of tellurium, from Sweden, by Berzelius, and in which he discovered selenium, I subjoin as an example of his method of proceeding for the

detection of selenium (CHILDREN'S *Translation of THENARD on Analysis*, 408) :—

a. 100 parts of the purest portions of the mineral, carefully selected, were dissolved in boiling nitric acid, the solution diluted with boiling water, and filtered; the clear liquor gave a precipitate with solution of common salt, and the matter which remained on the filter was washed with boiling diluted nitric acid, as long as the washings were rendered turbid by solution of sea-salt.

The chloride of silver, after being washed, dried, and fused, weighed 50.7 parts, equal to 38.93 of silver. The substance remaining on the filter consisted of silica and stony matter, and weighed, after being heated, 4 parts.

b. The liquid from which the silver had been separated was precipitated by sulphuretted hydrogen gas; the precipitate redissolved in aqua regia, and the solution concentrated till the nitric acid was entirely decomposed. It was then diluted with water, and sulphite of ammonia added, when the liquid gradually became turbid, and acquired a cinnabar red colour. After some hours it was boiled, and small portions of sulphite of ammonia added from time to time. The boiling was continued two hours, in order to precipitate the whole of the selenium; collected, dried, and heated nearly to fusion on the filter, it weighed 26 parts.

c. From the liquid, separated from the selenium, and deprived of its sulphurous acid by boiling, subcarbonate of potassa threw down a green precipitate, which, when washed, dried, and heated red, was converted into black oxide of copper, and weighed 27 parts, equivalent to 21.55 of copper. This oxide, dissolved in muriatic acid, gave a blue solution, with an excess of ammonia. The alkaline liquor, from which the carbonate of copper had been separated, still retained a greenish tinge; it was concentrated and slightly acidulated with muriatic acid, and a further precipitate of 1.5 part of copper separated by a plate of iron, which makes the whole of the copper 23.05.

d. The liquid, precipitated by sulphuretted hydrogen (*b*), was deprived of the excess of gas by boiling, and mixed with caustic ammonia, which threw down a yellowish precipitate, weighing, when dried, 1.8 parts, and was a mixture of oxide

of iron with a little alumina. The remaining solution was mixed with subcarbonate of potassa in excess, and evaporated to dryness. The saline mass, redissolved in water, left a white earth, which, heated red, weighed 3.4 parts. Sulphuric acid, mixed with this earth, occasioned an effervescence, and by evaporation became gelatinous, and deposited silica; it appeared also to contain magnesia, but it was not particularly examined, as these earths were evidently foreign to the ore.

The results of the analysis then are,

Silver	38.93
Copper	23.05
Selenium	26.00
Earthy and foreign substances	8.90
Loss	3.12
						<hr/> 100.00

The loss must be partly attributed to the carbonic acid of the carbonate of lime; still more to selenium, which it is difficult to separate entirely; and partly to the loss unavoidable in this sort of experiments.

Section XXII. OF THE COMBINATIONS OF ARSENIC.

THE method of separating arsenic from some of its combinations, and estimating its quantity has already been adverted to; some further account of the process, and of the analysis of arsenical combinations, remains to be given in this section.

Where the object is merely to drive off the arsenic contained in any ore, it may be effected by reducing it to powder, mixing it with saw-dust, or charcoal, and applying a dull red heat for some hours; the carbonaceous material, by keeping the arsenic in the metallic state, facilitates its escape in the form of vapour, and by dividing the material, prevents its running into lumps by partial fusion.

To estimate the quantity of iron in the *arsenical pyrites*, Messrs. Aikins advise the following as a short and convenient process: "Add to the powdered ore dilute nitric acid, and

digest in a gentle heat ; this will dissolve all the arsenic and iron, whilst most of the sulphur, with the siliceous residue, will remain undissolved. Pour off the nitrated solution, mix with it about twice as much powdered charcoal as the quantity of ore employed, and evaporate nearly to dryness ; put the residue into a tall crucible, and apply a brisk red heat for about ten minutes, by which time the arsenic will be almost entirely driven off in copious fumes, and the residue will consist of little else than charcoal and oxide of iron. Spread this upon a heated tile, till the charcoal is almost burned off, by which any arsenic still adhering will be dissipated, and the remaining oxide of iron may be reduced, or estimated, as mentioned under that metal. The nitrous acid is preferable to the muriatic in this process, as the latter, when strongly heated, volatilizes part of the iron, and renders the assay incorrect.”—*Dictionary*, i. 95.

In the analysis of ores containing arsenic, the most certain method of estimating its quantity, consists in acidifying it by nitric acid ; the arsenic acid may then be thrown down, with due precautions, by nitrate of lead, and the proportion of arsenic deduced from that of the arseniate of lead ; the following process, for instance, may be followed in the analysis of the *sulphuret of arsenic and iron* :

a. Digest 100 grains of the ore in fine powder, in nitric acid, a little diluted, so as sufficiently to moderate its action ; a portion of sulphur will remain undissolved, together with silica, if any be present, which may be separated, washed, and burned, in order to obtain the silica.

b. The acid solution containing nitric, sulphuric, and arsenic acids, and oxide of iron, may now be supersaturated with solution of soda, and the precipitate boiled in the alkaline liquor, which, being filtered off, leaves peroxide of iron, by which, when dried and ignited, the equivalent of the metallic iron in the ore is obtained.

c. Neutralize the filtered alkaline liquor with nitric acid, and pour in nitrate of lead, which will give a precipitate of sulphate of lead and arseniate of lead ; collect and wash it, and digest it in dilute nitric acid, which will take up the arseniate, but leave the sulphate of lead ; the arseniate may again be obtained by saturating with soda.

d. Estimate the sulphur in the sulphate of lead, and add it to that procured by process a. 100 parts of the arseniate of lead are equivalent to 56.5 of metallic arsenic?

Mr. Chenevix, in the *Philosophical Transactions* for 1801, has given some valuable details respecting the analysis of several ores of copper; the *native arseniate of copper* he examined as follows:

The ore was first heated to expel and estimate the water; it was then digested in dilute nitric acid, and nitrate of lead poured in, to form arseniate of lead, part of which being held in solution by excess of nitric acid, the liquor was evaporated nearly to dryness, and alcohol added, which occasioned the complete separation of the whole of the arseniate of lead; the remaining solution containing the copper was then boiled with potassa and the oxide of copper collected.

Pharmacolite, or *Native Arseniate of Lime*, was submitted to the following satisfactory analysis by Klaproth.—*Essays*, ii. 221.

a. 100 grains lost, by being moderately heated in a porcelain crucible, $22\frac{1}{2}$ grains. As, in this operation, neither by the smell nor by the sight, any volatilization of any principle could be observed, this loss of weight must have been caused by the escaping of the water of crystallization. On the other hand, the specimens had undergone no other change by this heating, except their surface being rendered a little duller. But the places spotted red from the cobaltic crust, had now assumed a light-bluish colour.

b. Those $77\frac{1}{2}$ grains, which remained after the ignition, dissolved in nitric acid, leaving a gray residue of 6 grains of siliceous, mixed with argillaceous, earth.

c. The filtered nitric solution, which somewhat inclined to the reddish, was evaporated to a smaller volume, and mixed with a solution of acetate of lead as long as any precipitation ensued. The precipitate, when collected, washed, and dried at a raised temperature, weighed 138 grains. It consisted of arseniated lead, = 46.5 grains arsenic acid.

d. What remained of the fluid after the separation of the precipitate, together with the washings, (c) was evaporated to some degree, during which, green-coloured borders appeared on the inner surface of the vessel. In order to separate the

small quantity of undecomposed acetate of lead it might yet have contained, I added the requisite quantity of muriatic acid. When, upon further evaporation, no muriate of lead any longer appeared, I mixed the fluid with sulphuric acid. This produced a copious precipitate of sulphated lime, which being collected on the filter, washed with weak spirit of wine, and heated to redness, weighed 54 grains. Therefore, since in 100 parts of ignited gypsum the pure calcareous earth amounts to $42\frac{1}{2}$ parts, the mentioned 54 grains determine the portion of lime contained in the fossil examined at 23 grains.

c. The remainder of the liquor was neutralized with carbonate of soda, and reduced to the state of siccity. On redissolving in water the dry saline mass, there remained a powder of the colour of flax-blossoms, and $\frac{1}{2}$ grain of weight, which tinged the borax-glass with a fine deep blue, and thus proved to be an oxide of cobalt.

Those 100 grains of pharmacolite, submitted to this analysis, have, therefore, been decomposed into

Acid of arsenic	46.50
Lime	23
Oxide of cobalt	0.50
Aluminous silex	6.
Water	22.50
					<hr/>
					98.50

But since the cobaltic oxide is here but casually admixed, as also the siliceous earth originates merely from the granitic matrix, it follows that, after subtracting these, the proportions of the constituent parts in the pure pharmacolite, are,

Acid of arsenic	50.54
Lime	25
Water	24.46
					<hr/>
					100.

Section XXIII. OF THE COMBINATIONS OF MOLYBDENUM.

THE *Native Molybdate of Lead* was analyzed nearly as follows by Mr. Hatchett :

a. The iron and molybdic acid were separated by the action of hot sulphuric acid ; the silica and lead (in the state of sulphate) were left undissolved.

b. The acid liquor, saturated by ammonia, deposited oxide of iron, which being separated, the whole was evaporated to dryness, and heated, to drive off sulphate of ammonia, and the dry residue was pure molybdic acid.

c. The undissolved residue of *a.* was boiled with carbonate of soda, and afterwards digested in dilute nitric acid : the carbonate of lead was dissolved, and the silica remained.

d. The nitrate of lead was decomposed by sulphuric acid, and when the sulphate of lead had been separated, the residual liquid was saturated with ammonia, which threw down a small additional portion of oxide of iron.

The results of this analysis were,

Molybdic acid	38.00
Oxide of lead	58.40
Oxide of iron	2.08
Silica	0.28
						<hr/>
						98.76

The analysis of the *sulphuret of molybdenum* may be performed by the action of nitric acid, which separates part of the sulphur, and acidifies the remainder, as well as the molybdenum ; the quantity of sulphur being ascertained by weighing the separated portion, and precipitating by nitrate of baryta that which is acidified, the loss of weight gives the proportion of molybdenum, and the excess of weight of the molybdic acid, above the deficiency, gives the proportion of oxygen united to the molybdenum to constitute molybdic acid. According to Bucholz, the sulphuret of molybdenum is composed of

Molybdenum	60
Sulphur	40
						<hr/>
						100

Section XXIV. OF THE COMBINATIONS OF CHROMIUM.

Two methods of analyzing *Chromate of Lead* have been pointed out by Vauquelin (*Journal des Mines*, No. 34). The first consists in repeatedly boiling the finely powdered ore in solution of carbonate of potassa, by which carbonate of lead and chromate of potassa are formed; and the second, by digesting it in muriatic acid, by which muriate of lead is produced, and the chromic acid obtained dissolved in the excess of muriatic acid.

Chromile of Iron is a more refractory compound, but it may be decomposed by the alternate action of potassa and muriatic acid (*Journal des Mines*, No. 55). The ore, in fine powder, should be heated red hot, with its weight of caustic potassa, for an hour, and the residue washed with water. The insoluble portion may then be boiled in muriatic acid, and, when no longer acted upon, washed, dried, and ignited as before; by the alternation of these processes, it will ultimately be resolved into an alkaline and acid solution; the former, neutralized by nitric acid, lets fall a portion of alumina and of silica, and holds chromate of potassa in solution; add to it nitrate of lead, by which chromate of lead is thrown down, and may be decomposed by muriatic acid. The muriatic solution, evaporated and diluted, lets fall silica, and ammonia throws down oxide of iron and alumina, which may be separated by potassa; evaporate to dryness, and heat to separate muriate of ammonia; the chromic oxide remains.

Section XXV. OF THE COMBINATIONS OF TUNGSTEN.

a. To ascertain the component parts of *Tungstate of Lime*, Klaproth digested 100 grains of it in fine powder with hot nitric acid, and then decanted the supernatant liquor from the yellow residue; upon which last, after edulcoration, he poured

liquid ammonia, and put it in a moderately warm place. This alkali took up that portion of the tungstic oxide, which had been set free by the nitric acid; and thus caused the yellow colour to disappear. The residue was treated twice more, by nitric acid and ammonia. In this way the total decomposition of the fossil was effected; so that only two grains of silica remained.

b. The nitric solution was then neutralized with ammonia. But as no change ensued, it was precipitated, in a boiling heat, with carbonated soda; and the precipitate washed and dried. It weighed 33 grains, and consisted of carbonate of lime, which, however, on redissolution in weak nitric acid, deposited one grain of silica. 33 grains of carbonate of lime are equivalent to 17.60 grains of lime.

c. The ammoniacal solution afforded, by evaporation in a low heat, slender needle-shaped crystals. When thoroughly desiccated the mass was ignited in a platinum crucible. The tungstic oxide which then remained had the form of a heavy, greenish-yellow powder, and weighed $77\frac{3}{4}$ grains.

Consequently the 100 grains of tungstate of lime have afforded

Yellow oxide of tungsten (tungstic acid)	. 77.75
Lime	. 17.60
Silica	. 3
	<hr/> 98.35

The examination of *wolfram* has not as yet been very satisfactorily accomplished, but the analysis of Messrs. D'Elhuyars is probably not far from the truth. (*Mémoires de l'Acad. de Toulouse*, ii.) Their result is as follows:—

Tungstic acid	. 64.0
Oxide of manganese	. 22.0
Oxide of iron	. 13.5
	<hr/> 99.5

Section XXVII. OF THE COMBINATIONS OF COLUMBIUM.

THE original analysis of the *Columbite* from North America, by Mr. Hatchett, is detailed in his paper in the *Phil. Trans.* for 1802.

This mineral, which is a compound of the oxides of columbium, iron, and manganese, was rendered soluble by the alternate action of fused carbonate of potassa and muriatic acid; the muriatic solutions contain the iron and manganese, and the columbium is retained in combination with the potassa, from which it may be precipitated by nitric acid.

Dr. Wollaston, in his experiments to show the identity of columbium and tantalum (*Phil. Trans.* 1809), fused 5 parts of the ore with 25 of carbonate of potassa, and 10 of borax. The resulting mass was softened with water and digested in excess of muriatic acid, which took up everything, except the oxide of columbium. The muriatic solution was neutralized with carbonate of ammonia, and the iron separated by succinate of ammonia; after which the manganese was separated by ferrocyanate of potassa. The results of this analysis are given above.

Section XXVIII. OF THE COMBINATIONS OF NICKEL.

THE separation of nickel from cobalt has already been described, and the analysis of meteoric iron has also been elsewhere adverted to. It remains here to give a general formula for the analysis of ores containing nickel, which is often rendered extremely complex, from the variety of substances united in some of its ores. The following general directions are extracted from Messrs. Aikin's *Dictionary* (ART. NICKEL), and the process has been repeated with sufficiently satisfactory results.

- i. The ore being ground to an impalpable powder must be

digested with nitric acid considerably diluted; nitrous gas will be given out, and by two or three digestions everything soluble will be taken up.

ii. The insoluble portion, consisting for the most part of sulphur and silix, is to be dried, weighed, and then heated; the sulphur (*a*) will burn off, and its amount may be ascertained by the difference of weight before and after ignition: the residue, after being boiled in a little nitric acid, is pure silix (*b*).

iii. Add together both the nitric solutions, nearly saturate the liquor with pure soda, evaporate it considerably, and then pour the solution into cold distilled water, by which the oxide of bismuth (*c*) will be precipitated.

iv. To the filtered solution add muriate of soda drop by drop as long as any precipitate falls down; this is muriate of silver (*d*).

v. Now evaporate the solution nearly to dryness, and boil it with strong nitric acid as long as any nitrous gas is given out: during the process red oxide of iron (*e*) will be precipitated.

vi. Having removed the oxide of iron, nearly saturate the liquor with soda, and pour in nitrate of lead as long as any arseniate of lead (*f*) is precipitated, which separate by the filter.

vii. The nitrous solution being now decomposed by carbonated soda, and the washed precipitate digested in liquid ammonia, oxide of iron (*g*) mixed with alumine (*h*) will be left behind, which may be separated in the usual way by potassa.

viii. The ammoniacal solution is to be slightly supersaturated with nitric acid, and a bar of iron being immersed in it will separate the copper (*i*); after which the liquor is to be decomposed by carbonated soda, and the precipitate again digested in ammonia, that the iron used for separating the copper may be got rid of.

ix. The solution, containing now only nickel and cobalt, is to be treated according to Mr. R. Phillips's (*Phil. Mag.* xvi. p. 312) method, as follows: Evaporate the liquor till the excess of ammonia is driven off, which may be known by the vapour ceasing to discolour moist turmeric paper; then largely

dilute it, and pour in pure potash or soda, as long as any precipitation takes place; what falls down is oxide of nickel (*k*).

x. The cobalt (*l*) alone remains in solution, and may be readily separated, by accurately saturating the liquor with nitric acid, and then adding carbonated soda.

The above general mode of proceeding is also applicable to the analysis of *nickel ochre*, except that it should first of all be digested in water, to dissolve out any sulphate of nickel which it may accidentally contain.

The results of the following analysis of the *crystallized sulphate of nickel*, which was made with a view to verify the equivalent number of the metal, are given above.

a. 100 grains of the crystals were heated in a porcelain crucible, to dull redness, for ten minutes; they crumbled into a pale green powder, perfectly soluble in water, consequently no acid had been expelled, and lost 45 grains = water of crystallization.

b. The remaining 55 grains of dry salt were dissolved in two ounces of water, to which nitrate of baryta was added, as long as it occasioned a precipitation; the sulphate of baryta thus formed being collected, washed, dried, ignited, and weighed, amounted to 83 grains = 28.25 sulphuric acid.

c. The filtered solution from which the sulphuric acid had been thrown down in the last process, was now mixed with a little sulphate of soda, to separate excess of baryta, filtered, concentrated by evaporating, and rendered alkaline by potassa; the precipitated oxide of nickel was then thoroughlyedulcorated, dried, and exposed to a dull red heat, till it ceased to lose weight; it amounted to 26.5 grains.

The salt, therefore, was thus decomposed into

Water of crystallization	45.00
Sulphuric acid	28.25
Oxide of nickel	26.50
	<hr/>
	99.75

Section XXIX. OF THE COMBINATIONS OF MERCURY.

WHAT is termed *native mercury* is usually an amalgam, containing a variable portion of silver, and often a trace of gold; it may be analyzed by exposure to heat, which dissipates the mercury, leaving silver and gold, separable by the action of dilute nitric acid.

If the amalgam, besides gold and silver, contain bismuth, its quantity may be judged of by solution in nitric acid, concentration by heat, and pouring the solution into a large quantity of pure water, by which the greater part of the bismuth will be thrown down in the form of white subnitrated oxide; but the analysis of complex amalgams is much simplified by previously expelling the mercury by heat, taking care that no other metal evaporates with it, which is sometimes the case at high temperatures.

The analysis of *Native Cinnabar* may be effected in the following manner:—

a. Reduce it to powder, and digest it in a sand heat with dilute nitro-muriatic acid; wash the insoluble portion with hot water, and add the washings to the solution; some sulphur will thus be separated, which may be dried and weighed, and some will be acidified, and may be precipitated by nitrate of baryta: it may possibly contain silica, and a little oxide of iron; if so, these are left after the combustion of the sulphur, and may be separated by dilute muriatic acid.

b. Add carbonate of potassa in excess to the nitric solution, collect and dry the precipitate, having previously boiled it for a minute or two in the alkaline liquor, and mix it with a little charcoal; put the mixture into a small coated retort, and at a red heat the mercury may be distilled over; the residue may be examined for alumina, lime, oxide of iron, or other extraneous matters.

The *Native Murio-sulphate of Mercury* may be dissolved in acetic acid, by which a portion of metallic mercury is usually separable from it; nitrate of baryta, added to the acetic solution, separates the sulphuric acid in the state of sulphate of

baryta, which being removed, nitrate of silver will throw down chloride of silver; immerse a plate of iron into the remaining solution to precipitate metallic mercury, or throw it down by carbonate of potassa, and distil with a little charcoal.

The *assay* of mercurial ores may be effected by mixing the powdered sample with half its weight of a mixture of equal parts of lime and iron filings, and submitting it to distillation in the open fire, in a coated glass retort.

Section XXIX. OF THE COMBINATIONS OF SILVER.

As instances of the analysis of complex silver ores, I have selected that of the bismuthic silver, and of the white silver ore, from Klaproth (*Essays*, i. 556, 145), whose paper on the composition of various silver ores may be strongly recommended to the attentive perusal of the student.

a. Upon 300 grains of the *Bismuthic Silver* from Schapbach, in the Black Forest, I poured three ounces of nitric acid, diluted with one of water; a great part of it dissolved, even in the cold; the residue was again digested with one ounce of the same acid, in a gentle heat; both solutions were filtered, mixed and evaporated to a smaller volume; during which process there separated some crystalline grains of nitrate of lead.

b. The concentrated solution had a greenish colour; when diluted with as much water as was requisite to redissolve that crystalline sediment, it was poured into a large quantity of distilled water; this immediately acquired a milky appearance, and deposited a white precipitate, which weighed 44.5 grains, when collected, lixiviated, and dried in the air, and proved, on further examination, to be oxide of bismuth.

c. Into the liquor that had been freed from this oxide, and was clear and colourless, I dropped muriatic acid, as long as it was rendered turbid by it: the precipitate did not appear to be mere muriate of silver, for this reason I digested it with nitric acid; a considerable portion was thus redissolved, and left pure horn-silver behind; which, upon careful collection,

and desiccation in a brisk heat, weighed 46 grains: thus, the portion of pure silver is determined at 34.5 grains.

d. The nitric acid, that had been affused upon the precipitate obtained by the muriatic *c*, yielded by dilution with much water 32 grains more of oxidized bismuth; which, with the preceding 44.5 *b*, gave together 76.5 grains.

e. The remainder of the fluid was farther reduced by evaporation, and in this process muriate of lead separated from it in crystals; this liquor was then combined with such a quantity of sulphuric acid as was requisite to decompose those crystals, and a second time evaporated; the precipitate which thence ensued was sulphate of lead, weighing 19 grains, when duly collected, washed, and dried.

f. What still remained of the solution, after its having been freed from the lead before contained in it, was saturated with caustic ammonia added in excess: in this way a brown ferruginous precipitate was produced, which was rapidly attracted by the magnet, and weighed 14 grains, when, after previous desiccation, it had been moistened with linseed oil, and well ignited: for these we must reckon 10 grains of metallic iron.

g. The liquor which had been supersaturated with ammonia, and which by its blue colour shewed that it held copper in solution, was next saturated to excess with sulphuric acid; on immersing then a piece of polished iron into it, two grains of copper were deposited.

h. The grey residue of the ore, that was left behind by the nitric acid *a*, weighed 178 grains; but when its sulphureous part had been deflagrated in a crucible gently heated, it weighed only 140.5 grains; this determines the portion of sulphur at 37.5 grains.

i. These 140.5 grains were digested with 3 ounces of muriatic acid in a heat of ebullition, and this process was repeated once more with 1.5 ounces. of the same acid; these solutions, by means of evaporation, yielded muriate of lead in tender spicular, and likewise in broad striated crystals; which, when again dissolved in the requisite quantity of boiling water, then combined with sulphuric acid, and evaporated, yielded 89 grains of sulphated lead: thus the whole quantity of this sulphate, including the 19 grains mentioned at *e*, amounted to

108 grains; for which, according to comparative experiments, 76 grains of reguline lead must be put in the computation.

k. That portion of the ore examined, which still remained after all the constituent parts beforementioned have been discovered, consisted merely of the gray quartzose matrix, the weight of which, in the ignited state, amounted to 70 grains.

Therefore those 300 grains of bismuthic silver ore mentioned above were decomposed into

Lead, <i>i</i>	76.
Bismuth, <i>d</i>	62.20
Silver, <i>e</i>	34.50
Iron, <i>f</i>	10.
Copper, <i>g</i>	2.
Sulphur, <i>h</i>	37.50
Quartzose matrix, <i>k</i>	70.
	<hr/>
	292.20

It follows, from this statement, that exclusively of the quartzose gangue, the constituent parts of the bismuthic silver are in the 100,

Lead	33.
Bismuth	27.
Silver	15.
Iron	4.30
Copper	0.90
Sulphur	16.30
	<hr/>
	96.50

Klaproth treated the *white silver ore* from Freyberg nearly as follows :

a. The ore was brittle, and easily levigated into a blackish powder.

b. Upon 400 grains in powder he poured 4 ounces of nitric acid, and 2 of water ; after sufficient digestion in a gentle heat, the solution was decanted, and the residue again treated with 2 ounces of the acid ; this mixture was next diluted with eight parts of water, and digested for some time ; he then separated the undissolved residue, consisting of a greyish-white powder, which, after washing and drying, weighed 326 grains.

c. The solution, which was nearly colourless, was combined with common salt, by which muriated silver was produced ; and the next day crystals of muriate of lead were found ; on

this, therefore, he boiled the whole precipitate in a large quantity of water, by means of which the muriated lead was redissolved, and separated from the muriate of silver, collected on the filter: this last, when reduced by fusion with soda, yielded 81.5 grains of reguline silver.

d. What remained of the solution, together with the liquor obtained by the decoction of the horn silver, he evaporated in part; and by adding a saturated solution of sulphate of soda, obtained from it 45 grains of sulphate of lead, which, upon reduction, afforded 32 grains of lead in the metallic state.

e. The remaining part of the solution was saturated with pure ammonia, upon which a light-brown precipitate fell, weighing 40 grains, whenedulcorated and ignited in a low heat; as that precipitate had the appearance of a mixture of iron and alumina, he dissolved it again in nitric acid, and precipitated first the iron by prussiate of potassa, and afterwards, by the addition of soda, a loose earth, which, when desiccated and ignited, weighed 28 grains, and upon trial with sulphuric acid, was found to be aluminous earth; this being subtracted from the above 40 grains, leaves 12 for the oxide of iron, which may be estimated at 9 grains of metallic iron.

f. After this the residue that remained from the solution of the ore, dissolved in nitric acid *b*, was subjected to a closer examination: Klaproth attempted to decompose it by muriatic acid, repeatedly poured upon it, and in every instance digested over it in a heat of ebullition. The process was rendered somewhat difficult by the crystals, which were deposited from the solution as soon as the heat fell below the boiling point; similar crystals likewise shot on the paper, through which the solution, though yet boiling, was filtered, and he gradually redissolved them in warm muriatic acid; at last there remained 51 grains of sulphur, leaving, after deflagration upon a test, two grains of a gray residue, one of which dissolved in muriatic acid, and was added to the preceding solution; the other grain was siliceous earth. The true quantity of the sulphur, therefore, amounted to 49 grains.

g. While the muriatic solution was cooling, it deposited a quantity of acicular crystals; these being separated, one half of the remaining fluid was distilled over in a small retort, and from the solution thus concentrated more crystals similar to

the first were deposited; this treatment was continued until no more crystals would form; when these crystals, collected together, were mingled with twice their weight of black flux, and reduced in an assay-crucible, thinly lined with charcoal-dust, they afforded $160\frac{5}{8}$ grains of lead; this lead, subjected to cupellation, emitted at the first application of heat a few antimonial vapours; it then fined quietly, and left a button of silver, weighing $\frac{1}{8}$ of a grain: this determines the proportion of lead at 160.25 grains; from which, however, a trifling quantity should be deducted for the portion of antimony before-mentioned, though it could not be well determined, besides that it could not weigh much above half a grain.

h. The fluid separated from the muriate of lead, concentrated, and diluted with a large quantity of water, deposited its metallic part, which, in the form of a subtle white powder, was only oxide of antimony, and being kneaded into a mass with soap, was reduced in a luted assaying-crucible, by means of black flux, into 28.5 grains of pure reguline antimony; some more small globules were found adhering to the lid of the vessel, of which I collected 3 grains; but still a small portion appeared to have escaped through the joinings, and for this reason, the true amount of antimony which I obtained may be reckoned at somewhat more than the 31.5 grains.

Hence the product of the 400 grains of the white silver ore here analyzed consisted of

Silver	$\left\{ \begin{array}{l} c \\ g \end{array} \right.$	$\left. \begin{array}{l} \\ \end{array} \right\}$	$\left. \begin{array}{l} 81\frac{1}{2} \\ \frac{1}{8} \end{array} \right\}$	$81\frac{5}{8} \text{ grs.}$
Lead	$\left\{ \begin{array}{l} d \\ g \end{array} \right.$	$\left. \begin{array}{l} \\ \end{array} \right\}$	$\left. \begin{array}{l} 32 \\ 160\frac{1}{4} \end{array} \right\}$	$192\frac{1}{4}$
Reguline antimony, <i>h</i>	.	.	.	$31\frac{1}{2}$
Iron, <i>e</i>	.	.	.	9
Sulphur, <i>f</i>	.	.	.	49
Alumina, <i>e</i>	.	.	.	28
Silex, <i>f</i>	.	.	.	1
				$392\frac{3}{8}$

Which in 100 parts makes

Silver	20.40
Lead	48.06
Antimony	7.88
Iron	2.25
Sulphur	12.25
Alumina	7.
Silex	0.25
	98.09

Section XXX. OF THE COMBINATIONS OF GOLD.

IN the Section on the combinations of Tellurium, I have quoted Klaproth's analyses of some of its ores containing gold; the only proper ore of this metal is *native gold*, which is occasionally found in veins, but of which by far the greatest proportion occurs dispersed in a granular form through certain alluvial strata. In this state silver and copper are the principal metals with which it is combined, and the analysis is sufficiently simple: the ore may be digested in nitromuriatic acid; the solution evaporated nearly to dryness, and again diluted, leaves the silver in the state of chloride; a strong solution of protosulphate of iron may then be used to throw down the gold, and the copper may be separated by immersing a plate of iron into the last filtered liquor.

If the proportion of silver and copper alloyed with the gold be considerable, the analysis may be simplified by using nitric acid in the first instance, which extracts the silver and copper, leaving the gold untouched: muriatic acid may then be poured in to throw down the silver, and the copper separated by iron, as before; or by precipitation by potassa, and ignition, which gives it in the state of peroxide.

Section XXXI. OF THE COMBINATIONS OF PLATINUM.

WE are indebted to Dr. Wollaston and to Mr. Tennant (*Phil. Trans.*, 1803,) for our knowledge of the component parts of the *ore of platinum*, as imported from South America. In this state it generally contains the following metals, exclusive of small particles of silica, and a variable portion of mercury; viz.; platinum, gold, palladium, rhodium, iridium, osmium, iron, copper, and lead; and the following is the process for their separation:

The mercury may be driven off by heat, a process which

renders the platinum yellower in consequence of the appearance of the grains of gold ; it may then be digested in nitro-muriatic acid diluted with its bulk of water, which takes up gold, iron, and a little platinum ; if the remaining ore be now digested in nitro-muriatic acid, by far the largest portion will be dissolved, and there will remain a black powder : to the nitro-muriatic liquor add a solution of muriate of ammonia, which will occasion the separation of the greater part of the platinum in the state of a very difficultly soluble ammonia-muriate, and which may be separated upon a filter ; in the filtrated liquor immerse a plate of zinc, which will throw down lead, rhodium, palladium, and a portion of platinum ; the lead may be separated by very dilute nitric acid ; dissolve the residue in nitro-muriatic acid, add common salt, and evaporate to dryness ; this residue, composed of the *soda-muriates of platinum, palladium, and rhodium*, is to be digested in alcohol, which dissolves the triple salts of platinum and palladium, but not that of rhodium, which therefore is thus separated : to the alcoholic solution add solution of muriate of ammonia, which throws down the platinum, and leaves the palladium in solution, which may be precipitated by ferrocyanate of potassa.

The insoluble black powder, by alternate fusions with potassa, and boiling in muriatic acid, is resolved into *osmium*, soluble in the alkali, and *iridium* in the acid. (*See the Sections on Platinum and its associates, in the preceding Chapter.*)

Section XXXII. OF SILICIOUS AND ALUMINOUS COMBINATIONS.

THE ready solubility of silica by fusion with the fixed alkalis, and its insolubility in the greater number of the acids, render its separation in many cases of analysis extremely easy. Muriatic acid, under certain circumstances, is capable of retaining a considerable quantity of silica, and the solution, when evaporated, assumes a gelatinous appearance (see page 227) : if

ammonia be then added, and the whole evaporated and heated red-hot, the silica is obtained pure, and not again soluble in the acid.

Alumina, like silica, is soluble in potassa, and the addition of acids to the mixed alkaline solution throws down a compound which is not entirely decomposed by the action of those acids, which, under ordinary circumstances, readily dissolve alumina without acting upon silica; a circumstance of which it is necessary to be aware, in certain cases of analysis.

If silica is predominant in a stone, it is in general rendered easily soluble by heating it in fine powder with potassa; but there are some of the hard aluminous compounds which are very difficultly acted on in this way; Mr. Chenevix found minerals of this class were most readily attacked by borax. One part of the mineral in fine powder, mixed with about three parts of glass of borax, is to be strongly heated in a platinum crucible; the contents, when cold, are perfectly soluble by long digestion in muriatic acid; the addition of carbonate of ammonia throws down the dissolved earths, which may be collected, redissolved, and examined as usual. Sir H. Davy has, in similar cases, recommended the use of boracic acid. (*Phil. Trans.*, 1805.)

There are a few minerals which contain fluorine, the presence of which is ascertained by heating the substance in fine powder with sulphuric acid, either before or after its fusion with potassa, when vapours which act upon and corrode glass will be liberated. To ascertain the proportion of fluorine in a mineral, it may be fused with potassa, and treated by muriatic acid, to separate silica; to the remaining liquid add excess of carbonate of potassa, and filter, neutralize the filtrated liquor with muriatic acid, and add muriate of lime, which will occasion a precipitate of fluoride of calcium, the purity of which is to be ascertained, and the quantity of fluorine inferred from it.

Boracic acid, originally found in the *Boracite* by Westrumb, has also been discovered by Klaproth in *Datolite* and in *Botryolite*, and more lately by Arfwedson and Berzelius in the green *Tourmaline* and *Rubelite*. The following is a sketch of M. Arfwedson's analysis:—

A portion of the green tourmaline in fine powder, was

strongly heated for an hour, with four times its weight of carbonate of baryta; the mass was dissolved in muriatic acid, and the solution evaporated to dryness; water, acidulated with muriatic acid, then dissolved everything but the silica.

The baryta was separated from the solution by sulphuric acid, and the other earths, with the oxides of iron and manganese, by an excess of carbonate of ammonia; the solution being separated from the precipitate, and evaporated to dryness, a sulphate was obtained, which, when again treated with ammonia as before, dried, and heated red, redissolved in water without leaving any residuum; this solution was freed from its sulphuric acid by acetate of baryta, and the filtered liquid evaporated; a gummy mass was obtained, which, by calcination in a platinum crucible, was decomposed, and afforded a fused alkaline mass, which proved to be lithia. "I began to consider my work almost finished (adds M. Arfwedson), when, on drying and heating a portion of the alkaline solution, I observed, at the moment the mass began to fuse, that it swelled up like borax, and left a glass, after calcination, of the same appearance as vitrified borax; it was very probable, therefore, that the mineral contained boracic acid, and I ascertained it by heating the fused mass with muriatic acid, which gave me, by evaporation, a residue, partly soluble in alcohol, to which it imparted the property of burning with the greenish flame so characteristic of boracic acid."

To obtain the quantity of this acid, a portion of the mineral was fused with bisulphate of potassa; the mass boiled with alcohol, and the filtered liquid evaporated to dryness; a substance remained equal to 1.1 *per cent.* of the weight of the tourmaline, and having all the properties of boracic acid. (*Ann. de Chim.* vol. x. p. 98.)

To the above observations, I shall add, as specimens of practical analysis, two instances from Klaproth's *Essays*, viz., his analysis of the *Spinell* and of *Kryolite*:—

a. 100 grains of rough spinell from Ceylon, in picked crystals, previously pounded to a coarse powder in a steel mortar, were triturated with water to an impalpable powder in a grinding-dish made of flint; after the powder of the stone, which was again dried, had been gently ignited, it showed an increase of weight of nine grains, arising from the particles abraded from the substance of the grinding-vessel.

b. I then digested the powder with two ounces of muriatic acid; when the acid was evaporated nearly to dryness, I diluted the mass with water, threw it upon the filter, and saturated the yellow muriatic solution with caustic ammonia; a brown flocculent oxide of iron fell down, which, collected and ignited, weighed 1.25 grains.

c. The liquor separated from that precipitate was concentrated by evaporation, perfectly neutralized with muriatic acid, and lastly combined with dissolved oxalate of potassa; in consequence of this, oxalate of lime precipitated, which, when carefully collected, and heated to redness in the cavity of a compact piece of charcoal, with the assistance of the blow-pipe, afforded .75 of a grain of lime.

d. Upon the powder of the stone, extracted by the muriatic acid, was poured ten times its quantity of alkaline ley, one-half of which consisted of caustic potassa, which mixture being first evaporated to dryness in a silver vessel, was afterwards ignited during the space of an hour; when the mass had been again softened with hot water, it left on the filtering paper 54 grains of a yellow residue when dried in the air.

e. These 54 grains were a second time mixed, and inspissated with a tenfold quantity of the same caustic lixivium, and afterwards ignited; upon which the mass, softened again with water, deposited a residue of a fine pulverulent form, weighing 43 grains when dried in the air,

f. I then neutralized the yellow alkaline solution (*d* and *e*) by means of sulphuric acid, and by affusing more acid, made a clear solution of the precipitate, which then formed; carbonate of potassa added in a boiling state threw down from it a precipitate of a very great bulk, which, after edulcoration, was again dissolved in sulphuric acid: this solution exhibited a slimy toughness, but it became perfectly fluid, when exposed to a raised temperature, and deposited a subtle white powder, which, after washing and desiccation in the air, weighed 95 grains: the sulphuric acid fluid, when separated from it, was set aside for a time.

g. The above-mentioned 95 grains were then gently ignited with thrice their quantity of caustic potassa; when again liquefied with water, and filtered, there remained only a slight residue, which, after washing, dissolved in sulphuric acid, with the exception of a few remaining particles.

h. The portion taken up by the potassa in the alkaline solution *g*, was precipitated by means of sulphuric acid; but it dissolved again in the acid, when added to excess, and was afterwards precipitated by boiling with carbonated alkali; this precipitate, previously washed, was once more dissolved in sulphuric acid.

i. The whole of the sulphuric solutions, obtained at *f*, *g*, *h*, was evaporated to a smaller compass, the gelatinous consistence into which it congealed, showed that a separation of siliceous earth had taken place: it was, therefore, largely diluted with water, digested, and the silex collected upon the filter.

k. This done, the sulphuric solution was put in a state to crystallize, by dropping into it a solution of acetate of potassa, and evaporating it slowly; it yielded at first regular and pure crystals of alum; but as the solution assumed a green colour towards the end, I combined it with Prussian alkali; a trifling precipitation ensued, of which the oxide of iron could not be estimated more than at one-fourth of a grain; the solution, being now freed of its ferruginous ingredient, was next decomposed in a boiling heat by carbonated potassa, and the precipitate, when dissolved anew in sulphuric acid, was brought to a final crystallization, after which the alum then obtained was added to the foregoing.

l. I now proceeded to the analysis of the 43 grains, that were left undissolved by the caustic alkaline ley *e*. These readily dissolved in dilute sulphuric acid, leaving some siliceous earth behind; the solution, separated from this last, was then combined with a small portion of acetated potassa, and exposed to spontaneous crystallization by exhalation in the open air. At first there yet appeared some solitary crystals of alum; but afterwards it entirely shot into sulphate of magnesia (Epsom salt).

m. To separate the sulphated magnesia thus obtained, from the admixed alum, it was strongly ignited in a porcelain vessel during half an hour, and the saline mass afterwards softened in water, and filtered; the aluminous earth, separated by this management, was afterwards dissolved in sulphuric acid, and in the proper manner crystallized into concrete alum.

n. The pure solution of the sulphated magnesia was preci-

pitated in a boiling heat by means of vegetable alkali. The magnesian earth, thus obtained in a carbonated state, weighed 20.5 grains when washed and dried; but after strong ignition it weighed only 8.25 grains.

o. All the washings (of which that at *f*, on precipitating the sulphuric solution by carbonate of potassa, retained the yellow colour of the first solution) were together evaporated to a dry saline mass; when they had been redissolved in water, there still separated a little earth, which, along with the precipitate remaining at *g*, was ignited with caustic potassa, and then by sulphuric acid resolved into aluminous and siliceous earths.

p. The whole quantity of alum, obtained at *k*, *l*, *m*, and *o*, amounted to 665 grains. It was now dissolved in water, and in a heat of ebullition decomposed by carbonate of potassa. The aluminous earth thus obtained, when edulcorated with water, and dried in a moderate warmth, weighed 221 grains; but after being purified by digestion with distilled vinegar, and subsequent saturation with ammonia, and being again edulcorated, and at last subjected for half an hour to an intense red heat, it weighed no more than 74.5 grains.

q. I then ignited, for half an hour, the whole of the siliceous earth collected from *i*, *l*, *o*: its weight was 24.5 grains. Hence, subtracting the 9 grains which had been abraded from the flint-mortar *u*, there remained 15.5 grains belonging to the spinell.

From this analysis it follows, that the constituent parts of the spinell in the 100 are

Alumine, <i>p</i>	74.50
Silex, <i>q</i>	15.50
Magnesia, <i>n</i>	8.25
Oxide of iron	{	<i>b</i>	.	1.25	1.50
		<i>k</i>	.	0.25	
Lime, <i>c</i>	0.75
					<hr/> 100.50

The reason why, in this instance, there appears in the sum of the weights an excess of half a grain, rather than a loss, unavoidable in the usual course of such processes, is probably, that the ignition was not powerful enough to effect in those ingredients that high degree of dryness, which that stone possesses in its natural undecomposed state.

Analysis of the Kryolite; after some preliminary experiments, which taught him the existence of fluoric acid, soda, and alumina in this mineral, Klaproth proceeded as follows :

100 grains of triturated kryolite, to expel entirely the fluoric acid, were inspissated to dryness in a platinum crucible, with 300 grains of concentrated sulphuric acid. The residual mass, previously drenched with water, congealed on evaporation to a soft, granular saline mass, which readily liquefied in a little water.

ii. Caustic ammonia precipitated from the clear solution the aluminous earth weighing 46 grains, whenedulcorated and dried, but 24 grains when ignited. The solution of this earth, in dilute sulphuric acid, with the assistance of heat, and combined with a just proportion of potassa, shot into regular crystals of alum.

iii. The fluid, from which the alumina had been precipitated, was neutralized with acetic acid, then combined with acetated baryta, and filtered, to separate the barytic sulphate. The clear fluid was now wholly evaporated, its dry residuum ignited in a platinum crucible, redissolved, and, after being rendered free by filtration, from the few adhering coaly particles, a second time evaporated to perfect dryness. It thus afforded $62\frac{1}{2}$ grains of dry carbonate of soda, equal to 36 grains of pure soda. This, saturated with acetic acid, crystallized all to acetate of soda.

If now, from the quantity of the fossil employed, be subtracted the weight of alumina and soda obtained, the remainder will give the weight of the fluoric acid, including perhaps the water of crystallization: 100 parts of kryolite, therefore, consist of

Soda	36
Alumina	24
Fluoric acid, including the water	40
							<hr/> 100

Analysis of Soils.—From the details in the preceding sections, the general methods of separating the inorganic, ingredients of soils, and of determining their relative proportions, may be learned, and in the Chapter on Vegetable and Animal Substances, the properties of their organized contents are described.

The following general instructions upon this subject by Sir H. Davy, were appended by his permission to the Chapter on Geology, contained in the last edition of this Manual, and as that is here omitted, I have inserted them in the present Section. The reader is referred to the work from which they are extracted, for a variety of useful auxiliary information upon the subject generally.

“ In cases when the general nature of the soil of a field is to be ascertained, specimens of it should be taken from different places, two or three inches below the surface, and examined as to the similarity of their properties. It sometimes happens that upon plains the whole of the upper stratum of the land is of the same kind, and, in this case, one analysis will be sufficient; but in valleys, and near the beds of rivers, there are very great differences; and it now and then occurs that one part of a field is calcareous, and another part siliceous; and in this case, and in analogous cases, the portions different from each other should be separately submitted to experiment.

“ Soils, when collected, if they cannot be immediately examined, should be preserved in phials quite filled with them, and closed with ground-glass stoppers.

“ The quantity of soil most convenient for a perfect analysis, is from 200 to 400 grains. It should be collected in dry weather, and exposed to the atmosphere till it becomes dry to the touch.

“ The specific gravity of a soil, or the relation of its weight to that of water, may be ascertained by introducing into a phial which will contain a known quantity of water, equal volumes of water and of soil, and this may be easily done by pouring in water till it is half full, and then adding the soil till the fluid rises to the mouth; the difference between the weight of the soil and that of the water will give the result. Thus, if the bottle contains 400 grains of water, and gains 200 grains when half filled with water and half with soil, the specific gravity of the soil will be 2, that is, it will be twice as heavy as water; and if it gained 165 grains, its specific gravity would be 1.825, water being 1.000.

“ It is of importance that the specific gravity of a soil should be known, as it affords an indication of the quantity of animal and vegetable matter it contains ; these substances being always most abundant in the lighter soils.

“ The other physical properties of soils should likewise be examined before the analysis is made, as they denote, to a certain extent, their composition, and serve as guides in directing the experiments. Thus, siliceous soils are generally rough to the touch, and scratch glass when rubbed upon it ; ferruginous soils are of a red or yellow colour ; and calcareous soils are soft.

“ 1. Soils, though as dry as they can be made by continued exposure to air, in all cases still contain a considerable quantity of water, which adheres with great obstinacy to the earths and animal and vegetable matter, and can only be driven off from them by a considerable degree of heat. The first process of analysis is, to free the given weight of soil from as much of this water as possible, without, in other respects, affecting its composition ; and this may be done by heating it for ten or twelve minutes over an Argand's lamp, in a basin of porcelain, to a temperature equal to 300 Fahrenheit ; and if a thermometer is not used, the proper degree may be easily ascertained by keeping a piece of wood in contact with the bottom of the dish ; as long as the colour of the wood remains unaltered, the heat is not too high ; but when the wood begins to be charred, the process must be stopped. A small quantity of water will perhaps remain in the soil even after this operation, but it always affords useful comparative results ; and if a higher temperature were employed, the vegetable or animal matter would undergo decomposition, and, in consequence, the experiment be wholly unsatisfactory.

“ The loss of weight in the process should be carefully noted, and when in 400 grains of soil it reaches as high as 50, the soil may be considered as in the greatest degree absorbent, and retentive of water, and will generally be found to contain much vegetable or animal matter, or a large proportion of aluminous earth. When the loss is only from 20 to 10, the land may be considered as only slightly absorbent and retentive, and siliceous earth probably forms the greatest part of it.

“ 2. None of the loose stones, gravel, or large vegetable fibres should be divided from the pure soil till after the water is drawn off; for these bodies are themselves often highly absorbent and retentive, and, in consequence, influence the fertility of the land. The next process, however, after that of heating, should be their separation, which may be easily accomplished by the sieve, after the soil has been gently bruised in a mortar. The weights of the vegetable fibres, or wood, and of the gravel and stones, should be separately noted down, and the nature of the last ascertained; if calcareous, they will effervesce with acids; if siliceous, they will be sufficiently hard to scratch glass; and if of the common aluminous class of stones, they will be soft, easily cut with a knife, and incapable of effervescing with acids.

“ 3. The greater number of soils, besides gravel and stones, contain larger or smaller proportions of sand, of different degrees of fineness; and it is a necessary operation, the next in the process of analysis, to detach them from the parts in a state of more minute division, such as clay, loam, marl, vegetable and animal matter, and the matter soluble in water. This may be effected in a way sufficiently accurate, by boiling the soil in three or four times its weight of water; and when the texture of the soil is broken down, and the water cool, by agitating the parts together, and then suffering them to rest. In this case, the coarse sand will generally separate in a minute, and the finer in two or three minutes, whilst the highly-divided earthy, animal, or vegetable matter will remain in a state of mechanical suspension for a much longer time; so that, by pouring the water from the bottom of the vessel, after one, two, or three minutes, the sand will be principally separated from the other substances, which, with the water containing them, must be poured into a filter, and, after the water has passed through, collected, dried, and weighed. The sand must likewise be weighed, and the respective quantities noted down. The water of lixiviation must be preserved, as it will be found to contain the saline and soluble animal or vegetable matters, if any exist in the soil.

“ 4. By the process of washing and filtration, the soil is separated into two portions, the most important of which is generally the finely-divided matter. A minute analysis of the

sand is seldom or never necessary, and its nature may be detected in the same manner as that of the stones or gravel. It is always either siliceous sand, or calcareous sand, or a mixture of both. If it consist wholly of carbonate of lime, it will be rapidly soluble in muriatic acid, with effervescence; but if it consist partly of this substance, and partly of siliceous matter, the respective quantities may be ascertained by weighing the residuum after the action of the acid, which must be applied till the mixture has acquired a sour taste, and has ceased to effervesce. This residuum is the siliceous part; it must be washed, dried, and heated strongly in a crucible; the difference between the weight of it, and the weight of the whole, indicates the proportion of calcareous sand.

“ 5. The finely-divided matter of the soil is usually very compound in its nature: it sometimes contains all the four primitive earths of soils, as well as animal and vegetable matter; and to ascertain the proportion of these with tolerable accuracy, is the most difficult part of the subject.

“ The first process to be performed, in this part of the analysis, is the exposure of the fine matter of the soil to the action of muriatic acid. This substance should be poured upon the earthy matter in an evaporating basin, in a quantity equal to twice the weight of the earthy matter; but diluted with double its volume of water. The mixture should be often stirred, and suffered to remain for an hour, or an hour and a half, before it is examined.

“ If any carbonate of lime or of magnesia exist in the soil, they will have been dissolved in this time by the acid, which sometimes takes up likewise a little oxide of iron; but very seldom any alumina.

“ The fluid should be passed through a filter; the solid matter collected, washed with rain-water, dried at a moderate heat, and weighed. Its loss will denote the quantity of solid matter taken up. The washings must be added to the solution, which, if not sour to the taste, must be made so by the addition of fresh acid, when a little solution of prussiate of potassa and iron must be mixed with the whole. If a blue precipitate occurs, it denotes the presence of oxide of iron, and the solution of the prussiate must be dropped in till no farther effect is produced. To ascertain its quantity, it must

be collected in the same manner as other solid precipitates, and heated red; the result is oxide of iron, which may be mixed with a little oxide of manganese.

“ Into the fluid freed from oxide of iron, a solution of neutralized carbonate of potash must be poured till all effervescence ceases in it, and till its taste and smell indicate a considerable excess of alkaline salt.

“ The precipitate that falls down is carbonate of lime, it must be collected on the filter, and dried at a heat below that of redness.

“ The remaining fluid must be boiled for a quarter of an hour, when the magnesia, if any exist, will be precipitated from it, combined with carbonic acid, and its quantity is to be ascertained in the same manner as that of the carbonate of lime.

“ If any minute proportion of alumina should, from peculiar circumstances, be dissolved by the acid, it will be found in the precipitate with the carbonate of lime, and it may be separated from it by boiling it for a few minutes with soap lye, sufficient to cover the solid matter; this substance dissolves alumina, without acting upon carbonate of lime.

“ Should the finely-divided soil be sufficiently calcareous to effervesce very strongly with acids, a very simple method may be adopted for ascertaining the quantity of carbonate of lime, and one sufficiently accurate in all common cases.

“ Carbonate of lime, in all its states, contains a determinate proportion of carbonic acid, *i. e.*, nearly 43 *per cent.*, so that when the quantity of this elastic fluid, given out by any soil during the solution of its calcareous matter in an acid is known, either in weight or measure, the quantity of carbonate of lime may be easily discovered.

“ When the process by diminution of weight is employed, two parts of the acid and one part of the matter of the soil must be weighed in two separate bottles, and very slowly mixed together till the effervescence ceases; the difference between their weight before and after the experiment, denotes the quantity of carbonic acid lost; for every four grains and a quarter of which, ten grains of carbonate of lime must be estimated.

“ 6. After the calcareous parts of the soil have been acted

upon by muriatic acid, the next process is to ascertain the quantity of finely-divided insoluble animal and vegetable matter that it contains.

“ This may be done with sufficient precision, by strongly igniting it in a crucible over a common fire till no blackness remains in the mass. It should be often stirred with a metallic rod, so as to expose new surfaces continually to the air ; the loss of weight that it undergoes denotes the quantity of the substance that it contains destructible by fire and air.

“ It is not possible, without very refined and difficult experiments, to ascertain whether this substance is wholly animal or vegetable matter, or a mixture of both. When the smell emitted during the incineration is similar to that of burnt feathers, it is a certain indication of some substance, either animal or analogous to animal matter ; and a copious blue flame at the time of ignition, almost always denotes a considerable proportion of vegetable matter. In cases when it is necessary that the experiment should be very quickly performed, the destruction of the decomposable substances may be assisted by the agency of nitrate of ammonia, which at the time of ignition may be thrown gradually upon the heated mass in the quantity of 20 grains for every hundred of residual soil. It accelerates the dissipation of the animal and vegetable matter, which it causes to be converted into elastic fluids ; and it is itself at the same time decomposed and lost.

“ 7. The substances remaining after the destruction of the vegetable and animal matter, are generally minute particles of earthy matter, containing usually alumina and silica, with combined oxide of iron or of manganese.

“ To separate these from each other, the solid matter should be boiled for two or three hours with sulphuric acid, diluted with four times its weight of water ; the quantity of the acid should be regulated by the quantity of solid residuum to be acted on, allowing for every hundred grains two drachms, or 120 grains, of acid.

“ The substance remaining after the action of the acid, may be considered as siliceous ; and it must be separated, and its weight ascertained, after washing and drying in the usual manner.

“ The alumina, and the oxide of iron and manganese, if any exist, are all dissolved by the sulphuric acid ; they may be separated by succinate of ammonia, added to excess, which throws down the oxide of iron ; and by soap lye, which will dissolve the alumina, but not the oxide of manganese : the weights of the oxides ascertained after they have been heated to redness will denote their quantities.

“ Should any magnesia and lime have escaped solution in the muriatic acid, they will be found in the sulphuric acid ; this, however, is rarely the case ; but the process for detecting them, and ascertaining their quantities, is the same in both instances.

“ The method of analysis by sulphuric acid, is sufficiently precise for all usual experiments ; but if very great accuracy be an object, dry carbonate of potassa must be employed as the agent, and the residuum of the incineration must be heated red for a half hour, with four times its weight of this substance, in a crucible of silver, or of well-baked porcelain. The mass obtained must be dissolved in muriatic acid, and the solution evaporated till it is nearly solid ; distilled water must then be added, by which the oxide of iron and all the earths, except silica, will be dissolved in combination as muriates. The silica, after the usual process of lixiviation, must be heated red ; the other substances may be separated in the same manner as from the muriatic and sulphuric solutions.

“ This process is the one usually employed by chemical philosophers for the analysis of stones.

“ 8. If any saline matter, or soluble vegetable or animal matter is suspected in the soil, it will be found in the water of lixiviation used for separating the sand.

“ This water must be evaporated to dryness in a proper dish, at a heat below its boiling point.

“ If the solid matter obtained is of a brown colour and inflammable, it may be considered as partly vegetable extract. If its smell, when exposed to heat, be like that of burnt feathers, it contains animal or albuminous matter ; if it be white, crystalline, and not destructible by heat, it may be considered as principally saline matter.

“ 9. Should sulphate or phosphate of lime be suspected in

the entire soil, the detection of them requires a particular process upon it. A given weight of it, for instance 400 grains, must be heated red for half an hour in a crucible, mixed with one-third of powdered charcoal. The mixture must be boiled for a quarter of an hour in a half pint of water, and the fluid collected through the filter, and exposed for some days to the atmosphere in an open vessel. If any notable quantity of sulphate of lime (gypsum) existed in the soil, a white precipitate will gradually form in the fluid, and the weight of it will indicate the proportion.

“ Phosphate of lime, if any exist, may be separated from the soil after the process for gypsum. Muriatic acid must be digested upon the soil, in quantity more than sufficient to saturate the soluble earths; the solution must be evaporated, and water poured upon the solid matter. This fluid will dissolve the compounds of earths with the muriatic acid, and leave the phosphate of lime untouched.

“ It would not fall within the limits assigned to this Lecture, to detail any processes for the detection of substances which may be accidentally mixed with the matters of soils. Other earths and metallic oxides are now and then found in them, but in quantities too minute to bear any relation to fertility or barrenness, and the search for them would make the analysis much more complicated, without rendering it more useful.

“ 10. When the examination of a soil is completed, the products should be numerically arranged, and their quantities added together, and if they nearly equal the original quantity of soil, the analysis may be considered as accurate. It must, however, be noticed, that when phosphate or sulphate of lime are discovered by the independent process just described (9), a correction must be made for the general process, by subtracting a sum equal to their weight from the quantity of carbonate of lime, obtained by precipitation from the muriatic acid.

“ In arranging the products, the form should be in the order of the experiments by which they were procured.

“ Thus, I obtained from 400 grains of a good siliceous sandy soil, from a hop garden near Tunbridge, Kent,

	Grains.
Of water of absorption	19
loose stones and gravel, principally siliceous	53
undecompounded vegetable fibres	14
fine siliceous sand	212
minutely divided matter, separated by agitation and filtration, and consisting of	
Carbonate of lime	19
Carbonate of magnesia	3
Matter destructible by heat, principally vegetable	15
Silica	21
Alumina	13
Oxide of iron	5
Soluble matter, principally common salt and vege- table extract	3
Gypsum	2
	<hr/> 81
Amount of all the products	379
Loss	21

“ The loss in this analysis is not more than usually occurs, and it depends upon the impossibility of collecting the whole quantities of the different precipitates, and upon the presence of more moisture than is accounted for in the water of absorption, and which is lost in the different processes.

“ When the experimenter is become acquainted with the use of the different instruments, the properties of the re-agents, and the relations between the external and chemical qualities of soils, he will seldom find it necessary to perform, in any one case, all the processes that have been described. When his soil, for instance, contains no notable proportion of calcareous matter, the action of the muriatic acid (7) may be omitted. In examining peat soils, he will principally have to attend to the operation by fire and air (8); and in the analysis of chalks and loams, he will often be able to omit the experiment by sulphuric acid (9).

“ In the first trials that are made by persons unacquainted with chemistry, they must not expect much precision of result. Many difficulties will be met with: but in overcoming them, the most useful kind of practical knowledge will be obtained; and nothing is so instructive in experimental science, as the detection of mistakes. The correct analyst ought to be well grounded in general chemical information; but, perhaps,

there is no better mode of gaining it, than that of attempting original investigations. In pursuing his experiments, he will be continually obliged to learn the properties of the substances he is employing or acting upon; and his theoretical ideas will be more valuable in being connected with practical operations, and acquired for the purpose of discovery.

“Plants, being possessed of no locomotive powers, can grow only in places where they are supplied with food; and the soil is necessary to their existence, both as affording them nourishment, and enabling them to fix themselves in such a manner as to obey those mechanical laws by which their radicles are kept below the surface, and their leaves exposed to the free atmosphere. As the systems of roots, branches, and leaves, are very different in different vegetables, so they flourish most in different soils; the plants that have bulbous roots require a looser and a lighter soil than such as have fibrous roots; and the plants possessing only short fibrous radicles demand a firmer soil than such as have tap roots, or extensive lateral roots.

“A good turnip soil from Holkham, Norfolk, afforded me eight parts out of nine siliceous sand; and the finely-divided matter consisted

Of carbonate of lime	63
silica	15
alumina	11
oxide of iron	3
vegetable and saline matter	5
moisture	3

“I found the soil taken from a field at Sheffield-place, in Sussex, remarkable for producing flourishing oaks, to consist of six parts of sand, and one part of clay and finely-divided matter. And 100 parts of the entire soil, submitted to analysis, produced

	Parts.
Silica	54
Alumina	28
Carbonate of lime	3
Oxide of iron	5
Decomposing vegetable matter	4
Moisture and loss	3

“An excellent wheat soil, from the neighbourhood of West

Drayton, Middlesex, gave three parts in five of siliceous sand ; and the finely-divided matter consisted of

Carbonate of lime	28
Silica	32
Alumina	29
Animal or vegetable matter and moisture	11

“ Of these soils the last was by far the most, and the first the least, coherent in texture. In all cases the constituent parts of the soil which give tenacity and coherence are the finely-divided matters ; and they possess the power of giving those qualities in the highest degree when they contain much alumina. A small quantity of finely-divided matter is sufficient to fit a soil for the production of turnips and barley ; and I have seen a tolerable crop of turnips on a soil containing 11 parts out of 12 sand. A much greater proportion of sand, however, always produces absolute sterility. The soil of Bagshot heath, which is entirely devoid of vegetable covering, contains less than $\frac{1}{20}$ of finely-divided matter. 400 parts of it, which had been heated red, afforded me 380 parts of coarse siliceous sand, 9 parts of fine siliceous sand, and 11 parts of impalpable matter, which was a mixture of ferruginous clay, with carbonate of lime. Vegetable or animal matters, when finely divided, not only give coherence, but likewise softness and penetrability ; but neither they, nor any other part of the soil, must be in too great proportion ; and a soil is unproductive if it consist entirely of impalpable matters.

“ Pure alumina or silica, pure carbonate of lime, or carbonate of magnesia, are incapable of supporting healthy vegetation.

“ No soil is fertile that contains as much as 19 parts out of 20 of any of the constituents that have been mentioned.

“ It will be asked, are the pure earths in the soil merely active as mechanical or indirect chemical agents, or do they actually afford food to the plant ? This is an important question ; and not difficult of solution.

“ The earths consist, as I have before stated, of metals united to oxygen ; and these metals have not been decomposed ; there is consequently no reason to suppose that the earths are convertible into the elements of organized compounds, into carbon, hydrogen, and azote.

“ Plants have been made to grow in given quantities of earth. They consume very small portions only ; and what is lost may be accounted for by the quantities found in their ashes ; that is to say, it has not been converted into any new products.

“ The carbonic acid united to lime or magnesia, if any stronger acid happens to be formed in the soil during the fermentation of vegetable matter, which will disengage it from the earths, may be decomposed : but the earths themselves cannot be supposed convertible into other substances, by any process taking place in the soil.

“ In all cases the ashes of plants contain some of the earths of the soil in which they grow ; but these earths, as may be seen from the table of the ashes afforded by different plants given in the last Lecture *, never equal more than $\frac{1}{30}$ of the weight of the plant consumed.

“ If they be considered as necessary to the vegetable, it is as giving hardness and firmness to its organization. Thus, it has been mentioned that wheat, oats, and many of the hollow grasses, have an epidermis principally of siliceous earth ; the use of which seems to be to strengthen them, and defend them from the attacks of insects and parasitical plants.

“ Many soils are popularly distinguished as *cold* ; and the distinction, though at first view it may appear to be founded on prejudice, is really just.

“ Some soils are much more heated by the rays of the sun, all other circumstances being equal, than others ; and soils brought to the same degree of heat cool in different times, *i. e.*, some cool much faster than others.

“ This property has been very little attended to in a philosophical point of view ; yet it is of the highest importance in agriculture. In general, soils that consist principally of a stiff white clay are difficultly heated ; and being usually very moist, they retain their heat only for a short time. *Chalks* are similar in one respect, that they are difficultly heated ; but being drier they retain their heat longer, less being consumed in causing the evaporation of their moisture.

* See Sir Humphry Davy's *Elements of Agricultural Chemistry*, 4to. p. 102.

“ A black soil, containing much soft vegetable matter, is most heated by the sun and air ; and the coloured soils, and the soils containing much carbonaceous matter, or ferruginous matter, exposed under equal circumstances to sun, acquire a much higher temperature than pale-coloured soils.

“ When soils are perfectly dry, those that most readily become heated by the solar rays likewise cool most rapidly ; but I have ascertained by experiment, that the darkest-coloured dry soil (that which contains abundance of animal or vegetable matter, substances which most facilitate the diminution of temperature), when heated to the same degree, provided it be within the common limits of the effect of solar heat, will cool more slowly than a wet, pale soil entirely composed of earthy matter.

“ I found that a rich black mould, which contained nearly $\frac{1}{4}$ of vegetable matter, had its temperature increased in an hour from 65° to 88° by exposure to sunshine ; whilst a chalk soil was heated only to 69° under the same circumstances. But the mould, removed into the shade, where the temperature was 62° , lost, in half an hour, 15° ; whereas the chalk, under the same circumstances, had lost only 4° .

“ Brown fertile soil, and a cold barren clay, were each artificially heated to 88° , having been previously dried ; they were then exposed in a temperature of 57° ; in half an hour the dark soil was found to have lost 9° of heat ; the clay had lost only 6° . An equal portion of the clay containing moisture, after being heated to 88° , was exposed in a temperature of 55° ; in less than a quarter of an hour it was found to have gained the temperature of the room. The soils in all these experiments were placed in small tin-plate trays, two inches square and half an inch in depth ; and the temperature ascertained by a delicate thermometer.

“ Nothing can be more evident, than, that the general heat of the soil, particularly in spring, must be of the highest importance to the rising plant. And when the leaves are fully developed, the ground is shaded ; and any injurious influence, which in the summer might be expected from too great a heat, entirely prevented : so that the temperature of the surface, when bare and exposed to the rays of the sun, affords at least

one indication of the degrees of its fertility ; and the thermometer may be sometimes a useful instrument to the purchaser or improver of lands.

“ The moisture in the soil influences its temperature ; and the manner in which it is distributed through, or combined with, the earthy materials, is of great importance in relation to the nutriment of the plant. If water is too strongly attracted by the earths, it will not be absorbed by the roots of the plants ; if it is in too great quantity, or too loosely united to them, it tends to injure or destroy the fibrous parts of the roots.

“ There are two states in which water seems to exist in the earths, and in animal and vegetable substances ; in the first state it is united by chemical, in the other by cohesive attraction.

“ If pure solution of ammonia or potassa be poured into a solution of alum, alumina falls down combined with water ; and the powder dried by exposure to air will afford more than half its weight of water by distillation ; in this instance the water is united by chemical attraction. The moisture which wood, or muscular fibre, or gum, that have been heated to 212° , afford, by distillation at a red heat, is likewise water, the elements of which were united in the substance by chemical combination.

“ When pipe-clay, dried at the temperature of the atmosphere, is brought in contact with water, the fluid is rapidly absorbed ; this is owing to cohesive attraction. Soils in general, vegetable and animal substances, that have been dried at a heat below that of boiling water, increase in weight by exposure to air, owing to their absorbing water existing in the state of vapour in the air, in consequence of cohesive attraction.

“ The water *chemically combined* amongst the elements of soils, unless in the case of the decomposition of animal or vegetable substances, cannot be absorbed by the roots of plants ; but that *adhering* to the parts of the soil is in constant use in vegetation. Indeed there are few mixtures of the earths found in soils that contain any chemically combined water ; water is expelled from the earths by most substances that combine with them. Thus, if a combination of lime and water be ex-

posed to carbonic acid, the carbonic acid takes the place of water, and compounds of alumina and silica, or other compounds of the earths, do not chemically unite with water; and soils, as it has been stated, are formed either by earthy carbonates, or compounds of the pure earths and metallic oxides.

“ When saline substances exist in soils, they may be united to water both chemically and mechanically; but they are always in too small a quantity to influence materially the relations of the soil to water.

“ The power of the soil to absorb water by cohesive attraction, depends in great measure upon the state of division of its parts; the more divided they are, the greater is their absorbent power. The different constituent parts of soils likewise appear to act, even by cohesive attraction, with different degrees of energy. Thus vegetable substances seem to be more absorbent than animal substances; animal substances more so than compounds of alumina and silica; and compounds of alumina and silica more absorbent than carbonates of lime and magnesia; these differences may, however, possibly depend upon the differences in their state of division, and upon the surface exposed.

“ The power of soils to absorb water from air is much connected with fertility. When this power is great, the plant is supplied with moisture in dry seasons; and the effect of evaporation in the day is counteracted by the absorption of aqueous vapour from the atmosphere, by the interior parts of the soil during the day, and by both the exterior and interior during night.

“ The stiff clays approaching to pipe-clays in their nature, which take up the greatest quantity of water when it is poured upon them in a fluid form, are not the soils which absorb most moisture from the atmosphere in dry weather. They cake, and present only a small surface to the air, and the vegetation on them is generally burnt up almost as readily as on sands.

“ The soils that are most efficient in supplying the plant with water by atmospheric absorption, are those in which there is a due mixture of sand, finely-divided clay, and carbonate of lime, with some animal or vegetable matter; and which are so loose and light as to be freely permeable to the atmosphere. With respect to this quality, carbonate of lime

and animal and vegetable matter are of great use in soils ; they give absorbent power to the soil without giving it likewise tenacity ; sand, which also destroys tenacity, on the contrary, gives little absorbent power.

“ I have compared the absorbent powers of many soils with respect to atmospheric moisture, and I have always found it greatest in the most fertile soils ; so that it affords one method of judging of the productiveness of land.

“ 1000 parts of a celebrated soil from Ormiston, in East Lothian, which contained more than half its weight of finely-divided matter, of which 11 parts were carbonate of lime, and 9 parts vegetable matter, when dried at 212° , gained in an hour by exposure to air, saturated with moisture, at temperature 62° , 18 grains.

“ 1000 parts of a very fertile soil from the banks of the river Parret, in Somersetshire, under the same circumstances, gained 16 grains.

“ 1000 parts of a soil from Mersea in Essex, worth 45 shillings an acre, gained 13 grains.

“ 1000 grains of a fine sand from Essex, worth 28 shillings an acre, gained 11 grains.

“ 1000 of a coarse sand, worth 15 shillings an acre, gained only 8 grains.

“ 1000 of the soil of Bagshot-heath gained only 3 grains.

“ Water, and the decomposing animal and vegetable matter existing in the soil, constitute the true nourishment of plants ; and as the earthy parts of the soil are useful in retaining water, so as to supply it in the proper proportions to the roots of the vegetables, so they are likewise efficacious in producing the proper distribution of the animal or vegetable matter ; when equally mixed with it they prevent it from decomposing too rapidly ; and by their means the soluble parts are supplied in proper proportions.

“ Besides this agency, which may be considered as mechanical, there is another agency between soils and organizable matters, which may be regarded as chemical in its nature. The earths, and even the earthy carbonates, have a certain degree of chemical attraction for many of the principles of vegetable and animal substances. This is easily exemplified in the instance of alumina and oil ; if an acid solution of alu-

mina be mixed with a solution of soap, which consists of oily matter and potassa, the oil and the alumina will unite and form a white powder, which will sink to the bottom of the fluid.

“ The extract from decomposing vegetable matter when boiled with pipe-clay or chalk, forms a combination by which the vegetable matter is rendered more difficult of decomposition and of solution. Pure silica and siliceous sands have little action of this kind; and the soils, which contain the most alumina and carbonate of lime, are those which act with the greatest chemical energy in preserving manures. Such soils merit the appellation which is commonly given to them of rich soils; for the vegetable nourishment is long preserved in them, unless taken up by the organs of plants. Siliceous sands, on the contrary, deserve the term hungry, which is commonly applied to them; for the vegetable and animal matters they contain not being attracted by the earthy constituent parts of the soil, are more liable to be decomposed by the action of the atmosphere, or carried off from them by water.

“ In most of the black and brown rich vegetable moulds, the earths seem to be in combination with a peculiar extractive matter, afforded during the decomposition of vegetables: this is slowly taken up, or attracted from the earths by water, and appears to constitute a prime cause of the fertility of the soil.

“ The standard of fertility of soils for different plants must vary with the climate; and must be particularly influenced by the quantity of rain.

“ The power of soils to absorb moisture ought to be much greater in warm or dry countries, than in cold and moist ones; and the quantity of clay, or vegetable or animal matter they contain, greater. Soils also on declivities ought to be more absorbent than in plains or in the bottom of valleys. Their productiveness likewise is influenced by the nature of the sub-soil or the stratum on which they rest.

“ When soils are immediately situated upon a bed of rock or stone, they are much sooner rendered dry by evaporation, than where the subsoil is of clay or marl; and a prime cause of the great fertility of the land in the moist climate of Ireland, is the proximity of the rocky strata to the soil.

“ A clayey subsoil will sometimes be of material advantage to a sandy soil ; and in this case it will retain moisture in such a manner as to be capable of supplying that lost by the earth above, in consequence of evaporation, or the consumption of it by plants.

“ A sandy or gravelly subsoil often corrects the imperfections of too great a degree of absorbent power in the true soil.

“ In calcareous countries, where the surface is a species of marl, the soil is often found only a few inches above the limestone ; and its fertility is not impaired by the proximity of the rock ; though in a less absorbent soil, this situation would occasion barrenness ; and the sandstone and limestone hills in Derbyshire and North Wales may be easily distinguished at a distance in summer by the different tints of the vegetation. The grass on the sandstone hills usually appears brown and burnt up ; that on the limestone hills, flourishing and green.

“ In devoting the different parts of an estate to the necessary crops, it is perfectly evident, from what has been said, that no general principle can be laid down, except when all the circumstances of the nature, composition, and situation of the soil and subsoil are known.

“ The methods of cultivation likewise must be different for different soils. The same practice which will be excellent in one case may be destructive in another.

“ Deep ploughing may be a very profitable practice in a rich thick soil ; and in a fertile shallow soil, situated upon cold clay or sandy subsoil, it may be extremely prejudicial.

“ In a moist climate where the quantity of rain that falls annually equals from 40 to 60 inches, as in Lancashire, Cornwall, and some parts of Ireland, a siliceous sandy soil is much more productive than in dry districts ; and in such situations wheat and beans will require a less coherent and absorbent soil than in drier situations ; and plants, having bulbous roots, will flourish in a soil containing as much as 14 parts out of 15 of sand.

“ Even the exhausting powers of crops will be influenced by like circumstances. In cases where plants cannot absorb sufficient moisture, they must take up more manure. And in Ireland, Cornwall, and the western Highlands of Scotland,

corn will exhaust less than in dry inland situations. Oats, particularly in dry climates, are impoverishing in a much higher degree than in moist ones."

Section XXXIII. OF THE COMBINATIONS OF ZIRCONIUM.

KLAPROTH'S description of the discovery of zirconia, and of the method of separating it from the Jargon and Hyacinth of Ceylon, contain a very instructive lesson in analytical chemistry; in those minerals the zirconia is combined with silica, and with a trace of oxide of iron; the following mode of obtaining pure zirconia, suggested by MM. Dubois and Silveira (*Annales de Chimie et Phys.* xiv.), furnishes, at the same time, a process for the analysis of the mineral, upon the whole less exceptionable than that of preceding chemists.

Reduce the zircons to fine powder, and heat them in a red heat for an hour, with two parts of pure potassa; pour distilled water on the fused mass, and wash the insoluble portion upon a filter; dissolve it in muriatic acid, and evaporate to dryness; pour water on the residue, which leaves silica, and dissolves muriate of zirconia and iron; filter, and add ammonia, which throws down zirconia and oxide of iron: wash the precipitate and boil it, while moist, in a solution of oxalic acid, which retains the iron, and forms an insoluble oxalate of zirconia; collect and edulcorate the latter, and heat it to redness in a platinum crucible: in this state the zirconia, though pure, is insoluble in acids; fuse it, therefore, with potassa, wash away the alkali, dissolve in muriatic acid, and precipitate by ammonia; the *hydrate of zirconia* now thrown down, when washed and dried, is pure and soluble.

Section XXXIV. OF THE COMBINATIONS OF GLUCINUM.

THE composition of the beryl, and of the emerald, and the mode of obtaining from them pure glucina, have been given above; in this section, therefore, I shall merely give Klaproth's examination of the emerald, as showing the mode of separating glucina in analyses. (*Essays*, ii. 177.)

a. 100 grains of light-green emerald were levigated in a flint mortar, by which their weight increased $2\frac{1}{2}$ grains. The powder of the stone was mixed with a solution of 250 grains of caustic soda, and inspissated in a silver crucible; upon which the dry mass was moderately ignited during 30 minutes.

b. When this mass had cooled, it appeared white, and not easily softened in water. It was saturated to excess with muriatic acid, which effected a solution. This, being evaporated, and afresh diffused in water, was thrown down upon the filter, in order to collect the siliceous earth, which, washed, dried, and ignited, weighed 68 grains, after deducting the $2\frac{1}{2}$ grains it received from the mortar.

c. The muriatic solution was supersaturated with soda and boiled. The precipitate was soon again taken up by the fluid, excepting some loose ash-gray flocks, which, upon drying and ignition, weighed $2\frac{1}{2}$ grains. As the filtering paper, upon which this residue has been collected, was coloured brownish, it was extracted with a little weak muriatic acid, and the solution treated with Prussian alkali, which produced a blue precipitate of iron.

d. Upon those $2\frac{1}{2}$ grains of the brownish residuum nitric acid was poured and again driven off by heat, after which potassa was affused. This took up but a little, and the residuum, again washed and ignited, lost only $\frac{3}{10}$ of a grain. The alkaline fluid was neutralized with nitric acid, and one-half of it combined with acetated lead, the other half with nitrate of silver. By the lead a lemon-yellow, and by the silver a brown-red precipitate was obtained. Thus the portion of chrome in emerald was separated and obtained singly.

e. The brown residue of d was dissolved in muriatic acid,

but the solution, acted on by a low heat, soon coagulated into a jelly-like substance, owing to the siliceous earth which separated, and upon ignition weighed half a grain. The fluid, freed from this, was then treated with a solution of succinate of soda. The precipitate, obtained by this means, when edulcorated and dried, gave one grain of oxide of iron.

f. As to the alkaline solution *c*, I mixed it with the remaining fluid of *e*, supersaturated the mixture with muriatic acid, and precipitated it in an ebullient heat with carbonated soda. The precipitate here obtained I dissolved in sulphuric acid, and after having combined it with acetate of potassa, forwarded it to crystallization. The first shootings yielded alum, in pure crystals; but on subsequent evaporation sulphate of lime appeared, which, in the ignited state, weighed $\frac{3}{4}$ of a grain, equivalent to $\frac{1}{4}$ of pure lime. What still remained of the fluid had now a thick oily consistence; diluted with a little water, and exposed to spontaneous crystallization, it afforded crystals, but they had not the form of alum.

g. This saline mass, together with the alum already obtained, was dissolved in water, and a large quantity of carbonate of ammonia affused, upon which I stoppered the vessel. After it had stood 24 hours, I separated the remaining earth by means of the filter, dissolved this last again in sulphuric acid, and, lastly, extracted it by adding a great over-proportion of carbonated ammonia. When the earth had again been separated, it was a second time subjected to the same treatment; after which, nothing more was taken up by the ammonia.

h. The aluminous earth was now heated to redness; it then amounted to $15\frac{3}{4}$ grains.

i. From the ammoniacal fluid, which had been collected from those reiterated extractions, the superabundant alkali was distilled off, until the quantity of the white earth, which parted from the fluid, no longer increased. This earth, washed and dried, weighed $23\frac{1}{2}$ grains; after ignition its weight proved to be $12\frac{1}{2}$ grains.

When redissolved in sulphuric acid, and left to spontaneous evaporation, it formed oblique, quadrilateral double pyramids, with truncated edges and corners. The saccharine taste of these crystals, in conjunction with their other properties,

showed that the base of this salt was glucine, the new earth discovered by Vauquelin in the beryl.

Hence this decomposed emerald has yielded, as its constituent parts,—

Silex	{	$\frac{b}{e}$	$\frac{68}{0.50}$	}	.	.	.	68.50
Alumine, <i>h</i>	15.75
Glucine, <i>i</i>	12.50
Lime, <i>f</i>	0.25
Oxide of iron, <i>e</i>	1
Oxide of chrome, <i>d</i>	0.30
								<hr/> 98.30

I have not been able to collect any information relative to the analysis of the compounds containing yttria, which would assist the student in their examination, in addition to that which has been given in the preceding Chapter, where I have enumerated the distinctive characters of yttria, and the mode of separating it from its combination with other earths.

CHAPTER VII.

OF THE ANALYSIS OF MINERAL WATERS.

THE following observations, relating to the analysis of mineral waters, have been drawn up principally with a view to facilitate the progress of the student, in that very difficult department of analytical chemistry. I have endeavoured to simplify the details by pointing out the readiest methods of recognising and separating the substances which usually occur, and have, therefore, omitted the enumeration of the more rare ingredients, or of those which are limited to particular places.

I have not adverted to the mode recommended by Dr. Murray (*Edinburgh Phil. Trans.*, viii.), because I cannot readily admit the existence of incompatible salts to the extent which his principle requires; nor do I think that it materially facilitates the analysis in those cases which present peculiar difficulties to the plan of determining the ingredients by evaporation.

Section I. OF THE TESTS AND APPARATUS REQUIRED
IN THE EXAMINATION AND ANALYSIS OF MINERAL
WATERS.

THOSE who have not access to a regular laboratory will find it convenient to arrange the following tests and re-agents in the manner represented in Plate I. of this volume: the larger phials should contain about 6 ounces by measure; the second size, 3 ounces; and the smallest, 1 ounce. Of these phials, the greater number should be simply stopped, and a few of them provided with an elongated stopper dipping into the fluid which they contain.

The larger phials may contain the following re-agents :—

Pure sulphuric acid.
 „ nitric acid.
 „ muriatic acid.
 Dilute sulphuric acid, 1 acid + 3 water.
 „ nitric acid „ „
 „ muriatic acid „ „
 Solution of potassa.
 „ soda.
 „ ammonia.
 „ carbonate of potassa.
 „ carbonate of soda.
 „ carbonate of ammonia.
 „ oxalic acid.
 „ oxalate of ammonia.
 „ baryta.
 „ acetate of baryta.
 „ nitrate of baryta.
 „ phosphate of soda.
 „ sulphate of silver.
 Alcohol.

The smaller phials may contain,

Tincture of galls.
 Solution of iodine in alcohol.
 „ nitrate of silver.
 „ ferrocyanate of potassa.
 „ muriate of lime.
 „ hydrosulphuret of ammonia.
 „ hydriodate of potassa.
 „ soap in alcohol.
 Chloride of platinum.
 Phosphorus.
 Sulphate of lime.
 Test-papers, turmeric, litmus, violet.
 Black flux.
 Nitrate of ammonia.

The tray should contain a few Florence flasks (1), Wedgwood and glass basins (2, 3), a platinum and a silver crucible (4, 5), a silver capsule (6), some funnels (7), test-glasses (8), test-tubes (9), and glass rods, filtering paper, a spirit (10) and an Argand lamp (11), a retort (12) and receiver (13), a copper basin to serve as sand-bath (14), a blow-pipe (15), a thermometer (16), a scale of equivalents (17), a dropping-bottle (18), a few watch-glasses (19), a support for holding glasses over a lamp (20), a small brass stand with rings (21), a tube, with a bulb in the centre and a pointed extremity, for

drawing up small portions of liquids (23), platinum pincers (24, 25); a small but good balance, with well-adjusted weights, is also requisite, accompanied by a phial and counterpoise for taking specific gravities; and, lastly, a small mercurial trough. There should also be a plentiful supply of distilled water, a portion of which should be contained in a dropping-bottle.

Section II. EXAMINATION OF MINERAL WATERS BY TESTS.

i. THE term *Mineral Water* is applied to those natural spring-waters which contain so large a proportion of foreign matter as to render them unfit for common domestic use, and to confer upon them a sensible flavour, and specific action upon the animal frame. Their temperature is liable to considerable variation, and is sometimes their principal character, as is the case with the waters of Bath and Buxton; but they are generally so far impregnated with acid or saline bodies, as to derive from them their peculiarities, and in this respect may conveniently be arranged under the heads of *carbonated*, *sulphureous*, *saline*, and *chalybeate* waters. See the annexed Table. The mere taste of the water enables us to determine to which of these subdivisions it probably belongs.

ii. In examining a mineral water, it is of importance to ascertain its specific gravity, which gives us some insight into the proportion of its saline ingredients, its specific weight, as compared with pure water, being of course augmented by its foreign contents. Mr. Kirwan (*Essay on Mineral Waters*, p. 145) has given the following formula for calculating the proportion of saline substances in a water of known specific gravity: “subtract the specific gravity of pure water from that of the water examined, and multiply the remainder by 1.4. The product is equal to the saline contents in a quantity of the water denoted by the number employed to indicate the specific gravity of distilled water. Thus, suppose the specific gravity of the water = 1.079, and that of pure water =

1.000, then $79 \times 1.4 = 110.6 =$ saline contents in 1000 of the mineral water."

This is a useful formula, but open to certain objections (Ure's *Dictionary*—Art. SALTS); and as it is often of considerable importance to acquire a just knowledge of the proportion of foreign bodies in water, it is advisable to conjoin the above method with the following:—

iii. Evaporate a given weight, say 1000 parts, to dryness, and expose the residue for 24 hours to a temperature not exceeding 300° upon a platinum capsule; weigh it while warm, and the mean obtained from this and the former experiment will give the proportion of dry saline ingredients within an error of 2 *per cent*. Thus, suppose 1000 parts of the above-mentioned water give by evaporation 114.4 dry residue, then $110.6 + 114.4 = 225 \div 2 = 112.5 =$ quantity of saline matter in a dry state (salts deprived of water of crystallization) existing in the mineral water under investigation.

iv. Having by these preliminary operations ascertained the relative *quantity* of foreign matter in the water under examination, the *nature* of the substances present is next to be inquired into.

The substances which have been found in mineral waters are extremely numerous*; those which very ordinarily occur, are the following:—

Oxygen.
Nitrogen.
Carbonic acid.
Sulphuretted hydrogen.
Carbonate of lime.
Carbonate of magnesia.
Carbonate of iron.
Muriate of magnesia.
Sea salt.
Sulphate of magnesia.
Sulphate of soda.
Sulphate of lime.

a. Oxygen and nitrogen exist in the greater number of spring waters in the proportions constituting atmospheric air; the proportion of nitrogen is, however, not unfrequently predominant. These gases give no peculiar flavour to the water.

* See the annexed analyses by Berzelius and Struve.

b. Carbonic acid renders mineral waters sparkling and effervescent: it is detected by occasioning a precipitate in aqueous solution of baryta, which dissolves with effervescence in dilute muriatic acid.

c. The presence of sulphuretted hydrogen is known by its peculiar disagreeable smell; by the production of a black precipitate on dropping into the water a solution of nitrate of silver; and by the deposition of sulphur on adding a few drops of nitric acid.

d. The carbonates are dissolved in the water by excess of carbonic acid, and consequently fall upon its expulsion by boiling. Carbonate of lime and magnesia are deposited in the form of a white precipitate. Carbonate of iron occasions the separation of a rusty brown ferruginous powder, and the water is blackened by a few drops of tincture of galls.

e. Mr. R. Phillips, in his analysis of Bath waters, has shown that the delicacy of galls, as a test for iron, is curiously affected by the presence of certain salts: if the iron be in the state of protoxide, its detection is facilitated by salts with a base of lime, and by alkalis; if in the state of peroxide, lime prevents the action of the test. This is well shown by dissolving a *very* minute portion of protosulphate of iron in a glass of distilled water, and adding a drop of tincture of galls, which occasions no immediate discoloration; but a drop of lime-water, or other alkali, instantly renders the presence of iron evident; so that the quantity of iron present in a water cannot be correctly judged of by the degree of precipitation occasioned in it by tincture of galls.

f. Ferrocyanate of potassa is also a good test to show minute quantities of iron in water, by the blue precipitate which it occasions; its action is aided by previously adding two or three drops of nitric acid to the water; but it is an equivocal test compared with galls.

g. The presence of muriatic salts and of chlorides, is indicated by a white cloud on adding sulphate of silver.

h. The sulphates, when present in water, afford a white precipitate on the addition of nitrate of baryta, which is insoluble in nitric acid.

i. Lime is recognised by a white cloud on dropping oxalate of ammonia into the water. A portion of the precipitate col-

lected upon leaf platinum, and heated before the blow-pipe, may be burned into quicklime.

k. Magnesia is rendered evident by adding carbonate of ammonia, which throws down the lime, and subsequently pouring in phosphate of soda, which, when magnesia is present, carries a portion of it down in the form of a granular precipitate of ammoniaco-magnesian phosphate.

Such are the readiest means of recognising the presence of the various substances that commonly occur, by the action of re-agents or tests; and, having gained such general information, we next proceed to the analysis of the water, in order to ascertain the relative proportions of the gaseous and saline ingredients which it holds dissolved.

Section III. ANALYSIS OF MINERAL WATERS.

v. To ascertain the relative proportions of the gaseous contents of water with perfect accuracy, is a very difficult undertaking, and rarely necessary; the following method is sufficiently precise in all ordinary cases of analysis. Provide a Florence flask capable of holding rather more than a measured wine-pint, which quantity of the water under examination is to be introduced into it, and a cork carefully fitted to its neck, through a perforation, in which is inserted a glass tube one-eighth inch diameter, rising perpendicularly about 18 inches, and then bent so as to pass conveniently under the shelf of the mercurio-pneumatic apparatus. (Where a sufficiency of mercury cannot be procured, warm water may be substituted, if only carbonic acid be present, and it may be absorbed by transferring the jar containing it to a solution of potassa.) The flask should be placed over an Argand lamp, and heat gradually applied till the water fully boils. The gas evolved is to be collected in the usual way, in a graduated jar over quicksilver, and submitted to the following examination:—

vi. Throw up a small quantity of solution of potassa, which, if carbonic acid be present, will absorb it, and the quantity will be shown by the diminution of bulk.

vii. Introduce the remaining air, or a portion of it, into a small bent tube, containing a bit of phosphorus; heat it so as to kindle the phosphorus, and note the diminution of bulk when cold. It is proportional to the oxygen present, and, if equal to one-fifth of the whole bulk, the gas may be regarded as atmospheric air*.

viii. If sulphuretted hydrogen be present it may be separated by strong alcoholic solution of iodine, which rapidly absorbs it, and scarcely takes up more than its own volume of carbonic acid gas. Chlorine, added to a mixture of sulphuretted hydrogen and carbonic acid, will also produce the absorption of the former if a little water be present; but it cannot be conveniently used over mercury.

ix. During the ebullition it not unfrequently happens that a precipitation ensues, indicating that the substances thrown down were dissolved by carbonic acid; and in that case they should be separated upon a filter *A*; after which the remaining water may be evaporated to dryness in a glazed porcelain basin; the dry residue transferred to a silver capsule, and perfectly desiccated at a temperature not exceeding 500°. *B*.

The precipitate *A* may consist of carbonate of lime, of carbonate of magnesia, or of oxide of iron; or it may be a mixture of the three; dissolve it in dilute muriatic acid, and add oxalic acid, which throws down oxalate of lime; separate this by filtration, and saturate the filtrated portion with carbonate of ammonia, which precipitates the peroxide of iron, and having removed this, evaporate the residuary mixture, and expose the dry salt to a red heat in a small platinum capsule; the magnesia, if any were present, will remain; if not, there will be no residue; for the oxalic acid and muriate of ammonia will be destroyed and volatilized.

100 parts of oxalate of lime indicate 77 of carbonate of lime.

100 parts of red oxide of iron indicate 90 of black oxide, or 143 of carbonate of iron. When carbonic acid holds iron in solution, the metal is in the state of protoxide, and if air be excluded, it requires long boiling to decompose it; for the same reason, if the water be exposed under the exhausted

* In separating oxygen, a solution of nitric oxide in protosulphate of iron may sometimes conveniently be employed, but it does not give so accurate a result as the action of phosphorus.

receiver of the air-pump, it does not readily become brown, as is the case when it is exposed to air; a drop or two of nitric acid facilitates the deposition of the red oxide.

100 parts of pure magnesia are equivalent to about 213 of carbonate of magnesia.

x. The dry residue B, is to be digested in six or eight parts of boiling alcohol, specific gravity 0.817, which will take up muriate of magnesia, and in some rare cases (where no sulphates are present) muriate of lime. Filter off the alcoholic solution, and wash the residue c with a little fresh alcohol, which add to the former, and evaporate to dryness D. The dry mass D, exposed for some time to a heat of 500° , is generally pure muriate of magnesia: if it contain muriate of lime, the latter earth may be separated by solution of oxalic acid, in the state of oxalate of lime.

I have found it, in some cases, convenient to convert the muriates of lime and magnesia into sulphates, by pouring upon them excess of sulphuric acid, evaporating to dryness, and heating the dry mass red hot. The sulphate of magnesia may then be almost completely separated from the sulphate of lime, by a small quantity of cold water; or a saturated solution of sulphate of lime may be used, which takes up the sulphate of magnesia, and, of course, leaves the sulphate of lime.

The alcohol will also take up a very minute portion of sea-salt, which, however, is too small to require estimation.

xi. The residue c, insoluble in alcohol, may contain sea-salt, sulphate of soda, sulphate of magnesia, and sulphate of lime; digest it in ten parts of boiling distilled water, which, when cold, will have taken up everything but sulphate of lime, of which an inappreciable portion only will have been dissolved; separate the solution into two equal portions, *a* and *b*.

To *a* add nitrate of silver, and wash and dry the precipitate, which is chloride of silver, D, and of which 146 parts indicate 60 of sea-salt.

To *b* add acetate of baryta as long as it occasions a precipitate, which is sulphate of baryta, E, and which is to be separated, dried, and weighed. 118 grains are equivalent to 72 of dry sulphate of soda, and to 60 of dry sulphate of magnesia.

In order to ascertain the quantity of magnesia present, and consequently the quantity of sulphuric acid belonging to it,

evaporate the liquid filtered off the barytic precipitate E to dryness; it will contain sea-salt, acetate of soda, acetate of magnesia, and, probably, a portion of the added acetate of baryta; ignite the dry mass, and wash it to separate the sea-salt and soda, magnesia and carbonate of baryta will remain insoluble, upon which pour dilute sulphuric acid; digest, filter, and evaporate the clear liquor to dryness; it is sulphate of magnesia, equivalent of course to the original portion of the salt; deduct the sulphuric acid contained in it from the whole in the precipitate E, and the remainder will give the quantity united to the soda.

xii. To estimate the quantity of sulphate of lime in the water, the residue of the evaporation of one pint may be washed with cold saturated solution of sulphate of lime, which will dissolve every thing but that sulphate, and which may thus be obtained and weighed; or, add oxalate of ammonia to a given quantity of the boiled and filtered water, collect the precipitate, and dry it at a heat of 500° . 64 grains of dry oxalate indicate 68 of dry sulphate of lime.

xiii. Such are the general components of mineral waters, and the means of ascertaining their relative quantities. Let us suppose the following results have been obtained, with a view to illustrate the mode of drawing up the analysis. By the process v., twelve cubical inches of gas have been expelled during the ebullition of a pint of water. The exposure to solution of potassa has occasioned a diminution of eleven cubical inches; which, it having been previously ascertained that no sulphuretted hydrogen was present, may be considered as carbonic acid. The remaining gas thrown up into a tube containing a portion of phosphorus, and heated, suffers scarcely any diminution, and the phosphorus does not burn: hence it may be regarded as nitrogen. The gaseous contents, therefore, of the water under examination are, in the wine-pint,—

Carbonic acid	11 cubic inches.
Nitrogen	1 ditto *

If sulphuretted hydrogen be present, it is best to have re-

* Of this nitrogen, a small portion will probably have been derived from the air in the tube connecting the flask with the pneumatic apparatus: a little practice soon enables the operator to ascertain when it has been expelled; or it may be received entire, and afterwards deducted from the whole produce.

course to a separate operation to estimate its quantity: for this purpose collect the gas as before, and throw up into it a small quantity of alcoholic solution of iodine. The absorption denotes the quantity of the gas. (viii.)

xiv. The next step of the operation relates to the examination of the precipitate deposited during ebullition. (ix. A.) Let us suppose the weight of oxalate of lime to be 3 grains, of oxide of iron 1.5 grain, and of magnesia 1 grain; then the above data give

Carbonate of lime	.	.	.	2.2 grains
„ iron	.	.	.	2.4
„ magnesia	.	.	.	2.1

xv. The alcoholic solution (x.) may be diluted with water and tested by oxalic acid for lime; if absent, evaporate to dryness as directed. Let us suppose the residue to be

Muriate of magnesia	.	.	.	5 grains.
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If the quantity of muriate of magnesia be considerable, greater accuracy is ensured by converting it into sulphate, which is done by placing it in a capsule of platinum, pouring upon it sulphuric acid, evaporating to dryness, and heating the dry mass to dull redness. 60 grains of this dry sulphate of magnesia indicate 102 of crystallized muriate of magnesia; hence the water under examination would have given 5.35 grains = 5 grains of muriate.

If the alcoholic solution contain muriate of lime, that earth must be previously separated by oxalic acid; and 82 parts of oxalate of lime (*dried at 100°*), are equivalent to 56 of dry muriate of lime (chloride of calcium).

xvi. The aqueous solution of the residue (c xi.) being divided into two portions, let us suppose the portion *a* xi. to afford 8.5 of chloride of silver, which indicates of sea-salt 3.5 grains = 7 grains in the pint.

xvii. Let us assume, that the precipitate of sulphate of baryta *b* xi. weighs 15 grains, indicating of

Sulphuric acid	.	.	.	5.1 grains.
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The process directed in xi. furnishes of

Sulphate of magnesia	.	.	.	3.75 grains,
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which contain 2.5 grains of sulphuric acid, and which deducted

from 5.1 grains leave 2.6 grains, which are adequate to the formation of

Sulphate of soda 4.65 grains.

So that the pint (the water having been divided into two equal portions) would contain of

Sulphate of magnesia . . . $3.75 \times 2 = 7.5$ grains.
 „ soda . . . $4.65 \times 2 = 9.3$ „

xviii. The addition of oxalate of ammonia, or oxalic acid, to a pint of the boiled water (xii.), furnishes a precipitate of 4.7 grains of oxalate of lime, indicating of

Sulphate of lime 5 grains.

xix. To give a general view, therefore, of the components of the mineral water which has thus been examined, we should place them as follows:—one wine pint contains—

Carbonic acid	11 cubic inches.
Nitrogen	1 „
Gaseous contents	<u>12</u>
Carbonate of lime	2.20 grains.
„ iron	2.40
„ magnesia	2.10
Muriate of magnesia	5.00
Sea-salt	7.00
Sulphate of magnesia	7.50
„ soda	9.30
„ lime	<u>5.</u>
Aggregate weight of solid contents	40.50

xx. Besides the substances now enumerated, and which may be considered as the most frequently occurring ingredients in mineral waters, there are others occasionally present, of which the following is an enumeration, with the best methods of detecting them:—

a. Carbonate of soda is known to exist in water, when, after having been boiled down to half its bulk, and, if necessary, filtered, it reddens turmeric paper, and restores the blue of litmus reddened by vinegar; it also affords an effervescent precipitate with nitrate of baryta, soluble in dilute nitric acid. This carbonate is incompatible with the soluble salts of lime.

Muriate of lime may also be used to detect the alkaline carbonates, with which it affords a precipitate of carbonate of lime. Carbonate of soda is distinguished from that of potassa,

by the latter affording a precipitate in neutral muriate of platinum, which the former does not. Carbonate of ammonia is obviously discoverable by its smell, when acted on by caustic fixed alkali or lime.

b. Silica is detected by evaporating the water to dryness, and boiling the residue in dilute muriatic acid. The silica, if present, remains as a white powder not altered by a red heat, but instantly fusing with a particle of carbonate of soda.

c. Boracic acid and borax have been found in certain lakes in India, and in some parts of Italy. To detect boracic acid, evaporate to one-eighth the original bulk of the water, and add carbonate of soda as long as it occasions any precipitate; boil and filter. The filtered liquor will contain borate of soda with some other salts of the same basis; evaporate to dryness in a platinum crucible, and digest the residue in three or four parts of sulphuric acid, diluted with its bulk of water. If boracic acid be present, it will separate in micaceous crystals.

d. Alumina has been found in a few mineral waters in the state of a sulphate. It may be separated by the following process: Evaporate to dryness, digest in alcohol, and redissolve the residue in eight parts of water; filter and add oxalic acid, which throws down lime, and which being separated, leaves magnesia and alumina in solution. Carbonate of ammonia throws down the alumina and leaves the magnesia.

Pure ammonia throws down both alumina and magnesia. These earths may be separated by solution of potassa, which dissolves the former but not the latter.

e. Manganese is sometimes found in water, but only in very small proportion, so as not to amount to more than a trace. Dr. Scudamore found a trace of manganese in the waters of Tunbridge Wells, and it has never been discovered in larger proportion.

f. It has been said that certain nitrates are occasionally present in water, but such solutions can scarcely be called *mineral waters*. If nitrate of lime be present, it will be taken up from the residue of evaporation by alcohol, and may be decomposed by carbonate of potassa, so as to afford carbonate of lime and crystals of nitre.

g. It sometimes happens that water contains lead, which may be detected by evaporation to one-eighth its bulk, adding a

few drops of nitric acid, and then hydriodate of potassa, which gives a yellow insoluble precipitate; and hydrosulphuret of ammonia, which forms a deep brown or black cloud. These precipitates may be reduced by heating them before the blow-pipe upon charcoal, mixed with a little black flux.

h. If vegetable or animal matter be contained in water, it gives it a brown colour, especially when evaporated. It may be destroyed in the dry residue by igniting it with a small addition of nitrate of ammonia.

The following analyses of mineral waters may be advantageously consulted by the student, as containing a variety of useful details, which are necessarily omitted in the above observations:—*Analysis of the Hot Springs at Bath*, by RICHARD PHILLIPS, Esq. *Analysis of the Brighton Chalybeate*, by Dr. MARCET. *Analysis of the Tunbridge Wells Waters*, by Dr. SCUDAMORE. Mr. CHILDREN'S *Translation of THENARD'S Essay on Chemical Analysis*, chap. vi. WALCKER *on the Bath Waters*. (*Quarterly Journal*, N. S.)

The annexed Tables shew the composition of the principal mineral waters of Europe. I have inserted Struve's analyses to shew the improvement which this branch of chemistry has received since the time of Bergman.

TABULAR VIEW
OF THE
COMPOSITION OF MINERAL WATERS.

TABULAR VIEW OF THE

One Pint (Wine Measure)

WATERS.		GASES.			CARBONATES.		
		Nitrogen C. I.	Carbonic Acid, C. I.	Sulphu- retted Hydrogen, C. I.	Carbonate of Soda, grains.	Carbonate of Magnesia, grains.	Carbonate of Lime, grains.
CARBONATED.	Seltzer	17.	4.	5.	3.
	Pyrmont	26.	10.	4.5
	Spa	13.	1.5	4.5	1.5
	Carlsbad	5.	5.	1.5
	Pouges	30.	10.	1.2	12.
	Saint Parize	22.	0.5	11.5
SUL- PHUROUS.	Harrogate	0.8	1.	2.3	0.7	2.5
	Moffatt	0.5	0.6	1.2
	Aix-la-Chapelle	5.5	12.	4.2
	Cheltenham Sulphur Spring	1.5	2.5
SALINE.	Seidlitz	2.5	0.8
	Cheltenham pure Saline
	Bristol	3.5	1.5
	Buxton	0.2	1.3
	Bath	1.2	0.8
	Scarborough	a trace
	Barege	uncertain	2.5	ditto
	Plombieres	2.2	0.3
	Kilburn	3.5	8.5?	0.5	1.
	Leamington New Bath	0.4	a trace	a trace
CHALY- BEATE.	Tunbridge	0.59	1.	{ a trace of oxygen }	0.03
	Cheltenham Chalybeate	2.5	0.5
	Brighton	2.2

COMPOSITION OF MINERAL WATERS.

contains the following Ingredients:

SULPHATES.			MURIATES.			Oxide of Iron.	Silica.	Tempe- rature.	Total of Saline Con- tents.	AUTHORITY.
Sulphate of Soda, grains.	Sulphate of Magnesia, grains.	Sulphate of Lime, grains.	Muriate of Soda, grains.	Muriate of Magnesia, grains.	Muriate of Lime.					
....	17.	Cold	29.	Bergman.
....	5.5	8.5	1.5	0.6	do.	30.6	Ditto.
....	0.2	0.6	do.	8.3	Ditto.
8.5	4.5	a trace	0.3	165°	19.8	Klaproth.
....	2.2	2.5	0.5	Cold	28.4	Hassenfratz.
....	13.	do.	25.	Ditto.
....	1.3	77.	11.	1.5	$\frac{1}{2}$	do.	94.	Garnet.
....	4.5	do.	4.5	Ditto.
....	5.	143°	21.2	Bergman.
23.5	5.	1.2	35.	0.3	Cold	65.	Parkes & Brande
....	180.	5.	4.5	$\frac{1}{2}$	do.	192.8	Bergman.
15.	11.	4.5	50.	do.	80.5	Parkes & Brande
1.5	1.5	0.5	1.	74°	6.	Carriek.
....	0.3	0.2	0.03	82°	1.83	Pearson.
1.5	9.	3.3	a trace	0.2	116°	14.6	Phillips.
20.	9.	ditto	Cold	2.9	Saunders.
....	a trace	0.5	120°	3.	Ditto.
2.3	1.5	0.3	?	66.	Vauquelin.
12.	37.	5.5	2.5	5.5	0.2	a trace	Cold	64.2	Schmeisser.
19.	14.	53.	1.5	0.8	do.	88.3	Lambe.
7.5	7.	18.	41.	do.	73.5	Ditto.
....	0.17	0.30	0.03	0.05	0.28	do.	0.56	Scudamore.
22.7	6.	2.5	41.3	0.8	do.	73.8	Parkes & Brande
....	4.	3.	0.75	1.4	0.14	do.	9.29	Mareet.

TABLE OF ANALYSES OF THE PRINCIPAL

INGREDIENTS FOUND IN 16 OUNCES OF WATER IN A DRY STATE, IN GRAINS.	CARLSBAD.	EMS.	MARIENBAD. Kreutzbr.	AUSCHOWITZ. Ferdinands- brunnen.
Carbonate of Soda	9.695	10.750	8.26	6.197
Sulphate of Soda	19.639	39.72	22.544
Muriate of Soda	7.975	7.634	12.45	8.996
Sulphate of Potash	0.540	0.93
Muriate of Potash	0.045
Carbonate of Lime	2.37	1.1407	4.1300	4.016
Sulphate of Lime
Sub-Phosphate of Lime	0.0017
Fluate of Lime	0.024	0.00192
Carbonate of Magnesia	1.369	0.7887	3.0560	2.4
Sulphate of Magnesia
Muriate of Magnesia
Nitrate of Magnesia
Alumina	0.0075
Sub-Phosphate of Alum	0.0024	0.0018
Carbonate of Strontian	0.007	0.0107
Sulphate of Strontian
Carbonate of Barytes	0.0029
Silica	0.577	0.4139	0.8800	0.669
Carbonate of Iron	0.0278	0.026	0.1760	0.4
Carbonate of Manganese	0.006	0.0037	0.0065	0.032
Total	41.9239	21.35932	69.616	45.314
Carbonic Acid Gas in 100 cubic inches .	53	51	125	149.56
Temperature (F.)	{ Sprud. 165° Neub. 138° Mühl. 128° Ther. 129°		53.°	49.°
Analyzed by	BERZELIUS.	STRUVE.	STRUVE.	STEINMANN.

MINERAL WATERS OF GERMANY.

EGER. Franzensbr.	PYRMONT.	SPA.	GEILNAU.	SELTERS.	SEIDSSCHUTZ.	PULLNA.
5.00	0.7375	6.6210	6.155
25.50	2.14566	0.0375	0.0420	23.4960	123.8
7.96	0.44949	0.5430	17.292
0.93	0.04194	0.07909	0.2872	0.397	4.8910	4.8
....	0.358
1.847	5.98824	0.9850	2.9705	2.1870	6.8060	0.77
....	7.22132	1.5050	2.6
0.014	0.01366	0.0156	0.0035
....	0.0018
0.600	0.32352	1.12273	2.1709	1.3780	1.0980	6.406
....	2.69752	83.1380	93.086
....	1.12664	1.6300	19.666
....	7.9070
....	0.0247
....	0.01473	0.00351	0.0027	0.0117
....	0.0192
....	0.02063	0.0463
....	0.0019
0.568	0.49639	0.4935	0.2695	0.302	0.1200	0.176
0.350	0.42346	0.3751	0.0127
0.006	0.04852	0.0519	0.0042
42.775	20.53412	4.35903	12.9288	28.0946	130.6315	251.3075
154	160	136	163.3	130	6.4	6.9
53.°	56.°	50.°	51.°	58.°	58.°	58.°
STRUVE.	STRUVE.	STRUVE.	STRUVE.	STRUVE.	STRUVE.	STRUVE.

CHAPTER VIII.

ON VEGETABLE SUBSTANCES.

HAVING in the preceding chapters considered the properties of the elementary substances, and such of their compounds as can be artificially formed, or are found in the mineral world, we proceed in this and in the succeeding chapter to examine the states of combination in which they occur in organic substances.

The several sections of the present chapter will relate to the formation of vegetable substances and their chemical physiology ; to the analysis of vegetable products, and the properties of their proximate component parts ; and to the phenomena and products of fermentation.

Section I. OF THE STRUCTURE AND GROWTH OF PLANTS,
AND OF THE CHEMICAL PHENOMENA OF VEGETATION.

IN examining the external structure of a perfect and full-grown vegetable, or plant, the essential organs of which it is observed to consist are the root, the stem, the leaves, the flowers, and the seeds.

The *root* serves to attach the plant to the soil, and is one of its organs of nutriment ; in its structure it closely resembles the stem, of which it may be regarded as a continuation, terminating in more or less minute ramifications, analogous to the branches deprived of leaves. The *stem* is usually erect and subdivided into *branches* which bear the *leaves* and *flowers*, and upon which the *seeds* are ultimately produced.

When a branch of a tree is cut transversely, it exhibits a

cortical portion, or *bark* ; *wood* ; and *pith*, or *central medullary substance*.

The bark is subdivisible into an external layer or *cuticle*, under which is a *cellular substance* lying upon the innermost part, or *cortical layers*.

The *cuticle* extends over every part of the plant ; it allows of absorption and transpiration, and being generally transparent, at least upon the leaves and flowers, it admits the influence of light. The cuticle varies in texture and appearance in different plants. On the currant and elder tree it is smooth and scales off : on the fruit of the peach, and on the leaf of the mullein, it is covered with wool ; on the leaf of the white willow, it is silky ; in several plants, it is covered with hair and bristles, which in the nettle are perforated, and contain a venomous fluid : on the plum and upon many leaves, it is varnished with a resinous exudation, which prevents injury from rain : it is fungous on the bark of the cork tree ; and on grasses, on the equisetum, and especially on different species of the rattan, it is covered with a glassy network of siliceous heart. This fact first occurred to Sir H. Davy in 1798, and led to experiments by which he ascertained that siliceous earth existed generally in the epidermis of the hollow plants. " It serves," he observes, " as a support, protects the bark from the action of insects, and seems to perform a part in the economy of those feeble vegetable tribes similar to that performed in the animal kingdom by the shell of the crustaceous insects."

Silica is also found in the hollow stem of the bamboo, constituting the substance, called *tabasheer*, the optical properties of which are peculiar, and have been described by Dr. Brewster. (*Phil. Trans.* 1819.)

Under the cuticle, or epidermis, is the *parenchyma* ; a soft substance, appearing under the microscope of a honeycombed or hexagonal cellular structure, resulting from the mechanical laws which influence the pressure of soft cylinders.

The *cortical layers* appear of a tabular and fibrous texture, and with the cellular substance receive and elaborate the sap. In the older branches and trunks of trees, the bark consists of as many layers as they are years old ; the innermost layer has been called the *liber*, in which the most essential vital func-

tions of the plant appear to go on, and by which a new layer of wood is annually secreted.

The *wood* consists of an outer stratum of living wood called the *alburnum*, or *sap-wood* ; and an inner dead part, or *heart-wood*. In the *alburnum*, which is tabular, the sap appears to rise from the roots ; it passes into the leaves, where it undergoes changes, and thence enters the vessels of the inner bark, in which new parts are produced, and which is thus enabled to generate new wood.

When the tubular structure is examined by a magnifier, it appears composed of vessels, some of which are simple, others perforated in various ways, and others spiral. The fibres of the wood consist of concentric and diverging layers, which have been called the *spurious* and the *silver grain*.

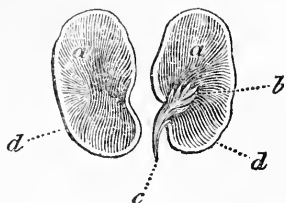
The *pith* occupies the centre of the wood ; it is very variable in quantity in plants of different ages, and appears not to be of essential importance. It probably sometimes serves as a reservoir of moisture.

The *leaves* are highly vascular, and appear composed of a woody skeleton, supporting a tabular and cellular structure. They allow of evaporation and absorption, and in them the sap is concocted and rendered fit for the production of new parts. The absorption and evaporation principally take place upon the lower surface of the leaf. In most plants the leaves are annually reproduced.

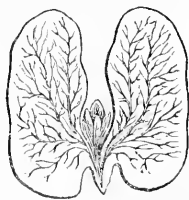
The *flower* consists of the *calyx*, or green support of the *corolla*, or *floral leaves* ; and of the *pistil* and *stamens*. The pistil is surmounted by the *style*, and is connected with a vessel containing the rudiments of the seeds. The stamens are surmounted by *anthers*, covered with a fine powder called the *pollen*, and which, being deposited upon the style, renders the seeds productive.

The *seed* is extremely various in form. It consists essentially of the *cotyledon*, the *plume*, and the *radicle*. The cotyledon contains the matter necessary for the early nutrition of the young plant. Sometimes it is single, sometimes double, and sometimes divisible into several lobes. The plume afterwards produces the stem and leaves, and is enveloped by the cotyledons ; the radicle generally projects a little, and when the seed

vegetates, it becomes the root. These parts are usually enveloped in a common membrane, and are well seen in the garden bean, represented in the annexed cut. *aa* are the cotyledons; *b* the plumula; *c* the radicle; *d d* the external membrane.



When a seed is placed under favourable circumstances the different parts begin to grow; the membranes burst, the plumula gradually expands and rises to the surface of the soil, and the radicle puts forth ramifications, and becomes a root. These changes constitute *germination*. The cotyledons, originally insipid and farinaceous, become sweet and mucilaginous, and furnish materials for the early nutriment of the young plant, before its root and leaves are adequate to their full functions; and vessels are observed ramifying throughout the cotyledons for this purpose, as here represented.



When the root and stem have acquired a certain degree of vigour, the cotyledons either rot away, or become leaves; and the plant then derives its nourishment by the absorbing powers of the root and leaves, the former collecting materials from the soil, the latter from the atmosphere.

The circumstances requisite for the healthy germination or growth of a seed are principally the following:—1. A due temperature, which is always above the freezing point, and below 100°. 2. Moisture in due proportion. 3. A proper access of air, the oxygen of which is slowly converted into carbonic acid. The joint operation of these agents also is required: for seeds exposed to air and moisture, but kept below 32°, will not grow, though they are not injured by the low temperature: nor will a seed vegetate without air, though moisture be present and a sufficient temperature; this is shown by burying seeds deep in the soil, and by the spontaneous vegetation upon newly-turned earth, in which seeds had existed, but through absence of oxygen had been unable to vegetate. Hence in all cases of tillage the seeds should be so sown as that the air may have access; in sandy soils this is

easily attained, but in clayey soils the adhesiveness of the materials is often the cause of their unproductiveness.

As the plant advances to perfection, it becomes dependant upon the air and soil for its nutriment : the roots absorb moisture and other materials ; and the leaves, while they exhale moisture, frequently absorb carbon from the carbonic acid present in the atmosphere, and evolve oxygen. (*Prefatory History of Chemistry*, p. ci.) This evolution of oxygen takes place while plants are exposed to the solar rays, and has by some been regarded as one of the efficient causes of the purification and renovation of the air. In the night-time, the leaves of plants always exhale carbonic acid, and at all times if the leaves be dying or unhealthy. There are also certain plants which appear under all circumstances rather to deteriorate than renovate the air ; on the whole, however, the balance is in favour of amelioration (Davy's *Agricultural Chem.* 4to. p. 195), though the supposed disappearance of the enormous quantities of carbonic acid gas continually pouring into our atmosphere, can scarcely be referred to the purifying action of vegetables. Upon this subject the reader will refer to the Constitution of the Atmosphere, and its Sources of Contamination, adverted to above. (Vol. i. p. 243.)

From M. Berard's experiments on the action of fruits upon air, (*Ann. de Chim. et Phys.* xvi.) it appears that they, in all cases, tend to the production of carbonic acid, and that this loss of carbon is essential to the ripening of the fruit ; for when deprived of oxygen the fruit dies. When fruits rot, they first change a portion of the surrounding oxygen into carbonic acid, and then liberate the same gas ready formed. He considers gum and lignin as the principles in unripe fruits which chiefly tend to the formation of sugar during their ripening, and has given several analyses of fruits in illustration of these views, a few of which are selected in the following Table : the elements of water are also probably concerned in the change.

	CHERRIES.		PLUMS.		PEACHES.		PEARS.		APRICOTS.		
	Green.	Ripe.	Green.	Ripe.	Green.	Ripe.	Green.	Ripe.	Green.	Riper.	Ripe.
	—	—	—	—	—	—	—	—	—	—	—
Vegetable albumen }	0.21	0.57	0.45	0.28	0.41	0.93	0.08	0.21	0.76	0.34	0.17
Colouring matter }	0.05	..	0.03	0.08	0.27	..	0.08	0.01	0.04	0.03	0.10
Lignin .	2.44	1.12	1.26	1.11	3.01	1.21	3.80	2.19	3.61	2.53	1.86
Gum . .	6.01	3.23	5.53	2.06	4.22	4.85	3.17	2.07	4.10	4.47	5.12
Sugar .	1.12	18.12	17.71	24.81	0.63	11.61	6.45	11.52	Trace	6.64	16.48
Malic acid	1.75	2.01	0.45	0.56	1.07	1.10	0.11	0.08	2.70	2.30	1.80
Lime . .	0.14	0.10	Traces	Traces	0.08	0.06	0.03	0.04	Trace	Trace	Trace
Water .	83.28	74.85	74.57	71.10	90.31	80.24	86.28	83.88	89.39	84.49	74.87

Under certain circumstances, the leaves of plants also *absorb* a considerable portion of aqueous vapour and water, as is shown by the resuscitation of a drooping plant, on sprinkling it with water, or exposing it to a humid atmosphere. It is probable that, in healthy vegetation, the absorption of water by the leaves takes place in the night season chiefly, and that their principal function in the day is that of transpiration. Upon these subjects the reader may consult Saussure's *Recherches Chimiques sur la Végétation*.

The fluid found in the vessels of plants is called their *sap*; it has a motion in the vessels, and appears to rise from the roots in a series of tubes in the alburnum; it then circulates in the leaves, becomes changed considerably in composition, and enters the vessels of the inner bark, enabling it to produce a new layer of wood, and to form the peculiar secretions which belong to it, and which, in smaller quantity, are also found in other parts of the vegetable.—See *Prefatory History of Chemistry*.

The cause of the motion of the sap has never been satisfactorily accounted for, though it is, perhaps, principally referable to the contraction and expansion produced by changes of temperature.

That the sap ascends in the *alburnum*, and descends in the *liber*, or inner bark, is shown by making an incision into the former and latter. The wound of the one will exude upon its

lower surface, and of the other upon its upper surface : and if a circular strip of bark be removed from a small branch of a tree near the stem, there will, of course, be an accumulation of sap in that branch, and its produce of leaves, flowers, and fruit, is often remarkably increased by such an operation.

If the alburnum, on the contrary, of a branch, be completely divided, it dies, as nourishment is then excluded ; a fact pointed out by Mr. Knight ; who has also shown, in proof of the situation of the vessels carrying the ascending sap, that coloured fluids applied to the root always pass upwards in the alburnum only.—*Phil. Trans.* 1801.

The sap of plants is of very various composition, and contains, besides certain proximate vegetable principles, several saline substances, especially the acetates of potassa and of lime : it also often exhibits traces of uncombined vegetable acids. The sap of the elm, beech, hornbeam, and birch, have been examined by Vauquelin (*Annales de Chimie*, xxxi.) : he found extractive and mucilaginous matter and acetic acid combined with potassa and lime. The solid matter afforded by their evaporation, yielded an ammoniacal smell, probably owing to albumen : the sap of the birch afforded saccharine matter. Dr. Prout has given some account of the sap of the vine. Its taste is sweetish, and its specific gravity scarcely exceeded that of water. Potassa and ammonia reddened it, and precipitated red flocks soluble in acetic acid. It was rendered slightly turbid by nitrate of silver, subacetate of lead, ferrocyanate of potassa, and oxalate of ammonia. It contained carbonic and acetic acids, and an alkali. (*Ann. of Phil.* v.) Professor Scherer analyzed the sap of the common maple : it had a milky appearance, and sweet taste. It did not affect litmus or turmeric. It was precipitated by oxalate of potassa, nitrate of silver, and baryta water. When evaporated, it yielded a salt, with base of lime, containing a peculiar acid, which he calls *aceric acid*. (Schweigger's *Journal*, iv.)

The sap of the rose tree has been examined by Mr. Addams. (*Quarterly Journal*, iv. 147, *N. S.*) In 12 fluid ounces he found

Oxalate of lime	2.900
Acetate of lime	1.097
Acetate of potassa	0.700
Gum and extractive	2.100
Sugar, &c. (soluble in alcohol)	0.100
Loss	0.353
		<hr/> 7.250

It is, however, almost impossible to collect the ascending sap without admixture of some other juices of the plant, so that the analyses only afford approximations to its real composition.

The *heat of plants* is in many instances above that of the surrounding medium, and there are cases on record in which a very marked elevation of temperature has been observed in them, but upon this subject we have as yet no accurate researches.—Smith's *Introduction to Botany*, p. 89.

Though the presence of light, air, and moisture, aided by a due temperature, are the principal requisites for the growth of plants, these are not the only essentials, for they also derive nutriment from the soil, which becomes impoverished by their growth, and ultimately incapable of supporting healthy vegetation, unless aided by *manures*. It is thus that the alkaline, earthy, and saline ingredients of plants are furnished, and quick-growing vegetables require a constant supply of these substances. *Manures* are of *vegetable*, *animal*, or *mineral* origin. The two former are capable of affording two of the essential ingredients of plants, namely, carbon and hydrogen; they may also yield some of the more immediate principles found in vegetables. The mere existence, however, of vegetable matter in the soil, is not sufficient to constitute it a manure; it must be reduced to a soluble state; to a state in which it can be absorbed by the roots of a growing vegetable; this is often effected by fermentation or putrefaction, or by applying the vegetable matter in a green state, as by ploughing in a green crop. Where the vegetable matter is in an inert insoluble form, it will be of no avail unless rendered active and soluble, which is effected either by mixing it with such kinds of animal matter as undergo quick putrefaction, and are themselves propitious to the growth of vegetables; such, for instance, as dung, rotten fish, or decaying parts of animals; or, by the operation of alkaline bodies, such as quicklime, &c.

When newly burned lime is strewed over a soil containing inert vegetable matter, it acts upon it, and renders it more or less soluble; while the lime, by absorbing moisture and carbonic acid, is slaked, and passes into the state of chalk, which is not hurtful to vegetables, and often a very useful addition to the soil: but when limestone contains magnesia, that earth remains caustic, and sometimes proves highly injurious.—Davy's *Agricultural Chemistry*, 4to. p. 234.

Section II. OF THE COMPOSITION AND ANALYSIS OF VEGETABLE SUBSTANCES, AND OF THEIR ULTIMATE PRINCIPLES.

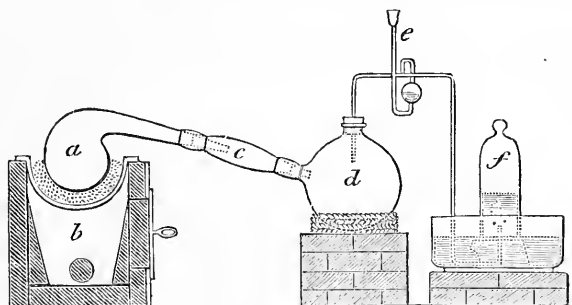
Of the ultimate Elements of Vegetable Products.

THE *ultimate* principles of vegetable substances are few in number; but by being combined in various proportions, they give rise to a series of compounds materially differing from each other, and which may be called their *proximate* component parts.

Carbon, hydrogen, and oxygen, are the principal ultimate components of vegetables: some afford nitrogen; in some there are traces of sulphur; and in their sap or juices we find small proportions of potassa and of lime, sometimes of soda and of magnesia: these bodies are combined with acids, and chiefly obtained by burning or incineration. It has already been said, that some plants contain silica; sulphate of lime is found in clover, nitrate of potassa in the sap of the sun-flower, and nitrate of soda in barley. Common salt is a very frequent ingredient in marine plants; phosphate of lime is found in oats and some other seeds; and nearly all vegetables yield traces of oxide of iron, and many of oxide of manganese. In Saussure's *Chemical Researches on Vegetation*, and in the fourth volume of Dr. Thomson's *System of Chemistry*, are copious tables, showing the earthy and saline constituents of vegetables.

When vegetable substances are submitted to *destructive distillation*, the carbon, hydrogen, and oxygen which they con-

tain enter into new arrangements, and a variety of *products* are obtained, differing in quantity and quality according to the nature of the vegetable substance, and varying with the mode of distillation. Water, empyreumatic oil, acids, carbonic oxide and acid, and carburetted hydrogen, are in this way formed; and, if the vegetable contain nitrogen, ammonia may be obtained. A portion of charcoal, with the saline and earthy ingredients, remains in the retort. By a careful analysis of these products, the relative proportions of carbon, hydrogen, and oxygen, and of nitrogen, if present, may be judged of. The following form of apparatus may be used in these researches :

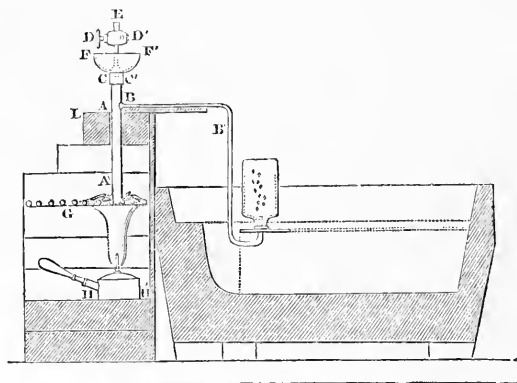


a is a glass or earthen retort, containing the vegetable substance to be decomposed, and placed in a sand heat upon the furnace *b*, which is gradually raised to a red heat. It is connected by the adapter *c* with the receiver *d*, which is kept cool for the condensation of the liquid products; the gases pass into the bell-glass *f* standing over mercury. *e* is a tube of safety, to allow for sudden expansion or contraction; there being in its lower part a small quantity of mercury which is occasionally elevated or depressed. The joints are secured by lute.

An improved mode of ascertaining the relative proportions of the ultimate component-parts of vegetable products has been devised by MM. Gay-Lussac and Thenard. (*Recherches Physico-Chimiques*, tom. ii.) It consists in burning the vegetable substance with chlorate of potassa. The requisite proportion of the chlorate, ascertained by previous experiment, is mixed with a given weight of the vegetable matter, and made into a small ball, which is dried, and burned in the apparatus described in the next page. The gases are collected over

mercury. The carbonic acid is absorbed by solution of potassa: if nitrogen be present, it will be found in the residuary gas; if carburetted hydrogen has been disengaged, its quantity and composition may be ascertained by detonation with oxygen. There should, however, always be allowance made for the production of excess of oxygen: thus the quantity of carbon is estimated from that of the carbonic acid formed; the quantity of hydrogen is deduced from that of the oxygen which has disappeared for the production of water; and the quantity of oxygen is learned by the remaining excess.

The details of the process will be found in the fourth volume of M. THENARD'S *Traité de Chimie*, with the following arrangement and description of the apparatus.



A hole is made through a brick, *L*, and the glass tube *AA* is passed through it as far as to the small lateral tube *BB*, which passes into the mercurial trough. The lower extremity of the tube rests upon the grate *c*, where it is to be heated red-hot by charcoal, inflamed by the lamp *II*. A brass cock is fitted, by grinding, to the tube *cc*. It has a solid plug, *DD*, in which is a cavity large enough to contain one of the balls to be analyzed, and which is introduced at the opening *E*. The plug is then turned round, and the ball falls into the red-hot part of the tube, where it burns, the gases passing into the mercurial apparatus. *FF* is a basin, into which ice may be introduced to keep the metallic parts of the apparatus cool. It is convenient to case the lower part of the tube *A* in iron, as it is sometimes blown out at that part by the expansion within.

Further directions respecting this process, with some observations upon it by Mr. Daniell, will be found in Mr. Children's translation of M. Thenard's volume on Analysis.

A simpler, and in most respects, preferable means of analyzing vegetable substances, consists in exposing them to heat with certain metallic oxides in vessels which admit of our collecting the residue and products of combustion. For this purpose, procure a copper tube, bored from a solid bar, about twelve inches long, and one-third of an inch internal diameter, with a bent brass tube ground to its open end, to which is attached, also by grinding, a glass tube containing powdered muriate of lime, and bent so as conveniently to pass under the shelf of the mercurio-pneumatic apparatus; the muriate of lime may be kept in its place by some loose amianthus, and the weight of the glass tube should be carefully ascertained. Fill the glass tube loosely with dry amianthus; weigh out 3 grains of the vegetable substance to be analyzed, and mix these intimately with 120 grains of finely-powdered peroxide of copper; put this mixture into the bottom of the copper tube, and afterwards fill it up loosely with oxide of copper; then attach the brass and glass tubes, and arrange the apparatus so that the open end of the latter may be brought under an inverted jar of mercury, and the copper tube placed in a small furnace and surrounded with burning charcoal, taking care to apply heat in the first instance to the upper part of it, and afterwards to the bottom containing the vegetable matter; care should be taken to make the whole of the copper tube gradually dull red, and to keep the brass tube as cool as possible by a damp cloth. During this operation the carbon of the vegetable matter will be converted into carbonic acid, and collected over the mercury; the nitrogen, if any, will be mixed with it, and the hydrogen will be converted into water, and absorbed by the muriate of lime. The carbonic acid may be absorbed by liquid potassa, and its bulk furnishes a datum upon which to calculate the proportion of carbon, while the increase of weight in the muriate of lime shows the quantity of water formed, and consequently the quantity of hydrogen in the matter subjected to analysis. If we find the aggregate weight of the carbon and hydrogen, or of the carbon, hydrogen, and nitrogen, equal to that of the original vegetable sub-

stance, no oxygen was present ; but if there be a deficiency it may be referred to oxygen.

In employing the peroxide of copper in these experiments, green glass tubes may, in most cases, be conveniently substituted for those of metal ; and they may be protected by an external case of copper foil, made by rolling a slip of the foil spirally round the tube, and securing its extremity by a twist of wire. The heat, also, may be conveniently applied by a spirit-lamp with a numerous series of wicks, as contrived by Mr. Cooper, to whose description of the apparatus, and of the requisite precautions in its employment, the reader is referred. (*Quarterly Journal*, xvii., p. 222.) An extremely convenient form of apparatus for the ultimate analysis of organic compounds, invented by Dr. Prout, is described in Henry's Chemistry (vol. ii.) ; but it is in great measure superseded by a more recent contrivance, which I shall presently describe.

In all these analyses the vegetable substance should either be previously perfectly dried, or the quantity of adhering water, if there be any, allowed for in summing up the results ; with every precaution, however, the method is open to objections, and liable to several sources of fallacy. Indeed, although I have frequently made such experiments with every possible caution, I have in few instances gained perfectly satisfactory results : the quantity of carbon may, it is true, be obtained with sufficient accuracy ; but the greatest difficulty attends the collection of the water which is formed, and the estimates that I have been able to make of the relative proportions of oxygen and hydrogen have sometimes been so exceedingly at variance in different trials, as to shake my confidence in the accuracy of the mode of analysis ; some difficulty also often occurs in respect to the nitrogen. When, therefore, I see the results of the analysis of a single grain of vegetable matter detailed to the third decimal number, I cannot but suspect that theory has more share in the result than experiment, more especially when such analysis is made the basis of an atomical calculation.

There are few chemists who have had more experience in this branch of analytical chemistry, or who are more competent to meet its difficulties, than Dr. Prout. In his communication to the Royal Society, "on the ultimate composition of simple alimentary substances, &c." he has thrown out

several valuable remarks upon the subject generally, and has described the following new forms of apparatus. (*Phil. Trans.*, 1827.)

There are two methods, he observes, of arriving at the quantity of water formed during the combustion of an organized substance; either actually to collect and weigh it, as Berzelius did, or to estimate the quantity by the loss of weight sustained by the tube after the combustion. The latter in general is the best. Whichever method is adopted, it obviously becomes necessary that no extraneous water be present; but all pulverulent substances, and oxide of copper among the rest, are more or less hygrometric, and rapidly attract moisture from the atmosphere. This circumstance seems to have struck the French chemists, and it occurred to Dr. Prout at a very early period. Dr. Ure, however, was the first who published a method of obviating this difficulty; and his method, if this were the only difficulty to contend with, is capable of considerable precision. But there is another, and perhaps still more troublesome property possessed by the oxide of copper, in common with many other powders, namely, that of condensing air as well as water*; and these two difficulties, taken together in conjunction with another mentioned in a note below, render great precision almost out of the question†. To conquer

* See Saussure's paper on the absorption of the gases by different bodies.—*Annals of Philosophy*, vi. 241. Also GILBERT'S *Annalen der Physik*, xlvii. 112.

† The important bearings of the remarks contained in the following note, are my apology for inserting it entire from Dr. Prout's paper.—“As I am unwilling that so much labour should be lost, particularly as it may be of some use to other inquirers, I have thrown into the form of a note a few of the principal circumstances connected with the enquiry mentioned in the text. In my earlier experiments tubes of iron, copper, &c. were employed instead of glass, and charcoal instead of spirits, as the medium of heat; and during this period most of the modifications of apparatus which have been since proposed as novelties or improvements, were tried and rejected. I first took the hint of employing a spirit-lamp from Mr. PORRETT, and was certainly among the first that did so employ it. Various forms of lamps were tried, but at length I was induced to relinquish the use of the horizontal apparatus for the vertical one; and this, I have no hesitation in saying, is by far the best form of apparatus hitherto proposed for the substances to which it is adapted; nor would any other have been required by me, at least, had it not been for the properties of the oxide of copper alluded to in the text, which render this and all other forms of apparatus depending on the employment alone of that substance perfectly useless when great accuracy is required. It has been objected

these, every means that could be thought of, as likely to succeed, were tried, but without effect. At length a method was adopted, founded on the following well-known principles.

When an organic product containing three elements, hydrogen, carbon, and oxygen, is burnt in oxygen gas, one of three things must happen. 1. The original bulk of the oxygen gas *may remain the same*, in which case *the hydrogen and oxygen in the substance must exist in it in the same proportions in which they exist in water* (for it is well known that oxygen gas by being converted into carbonic acid gas is not altered in

to the lamp that the heat produced by it is not sufficient ; but this is a mistake, at least I have never met with any substance that resisted its action, provided the oxide of copper was well shaken up in the tube, or, if necessary, taken out of the tube and retritured, and afterwards exposed to heat a second time, one or other of which *ought to be done in all instances*, whatever be the medium of heat employed ; for no ordinary heat will induce the oxide to part with its oxygen to a combustible substance at some distance off, and not immediately in contact with itself. A great heat is also attended with some disadvantages, and among others, that of causing the oxide to adhere together in hard and solid masses, which thus becomes more difficult to be removed from the tube, and much less adapted for future experiments. In general organized bodies are more difficult of combustion, and require more heat than crystallized ones. The lamp described in the text I have only recently employed, and it answers the purpose in all respects better than any I have yet seen.

With respect to the sources of error above-mentioned, it was found that 200 grains of the oxide of copper, recently ignited, gained, after ten or fifteen minutes' exposure to the air, a quantity varying from .02 to .05 grain, one half of which, or even more, was acquired before it became cold ; that is to say, before it had cooled down to 100°, considerably above which point it began to acquire weight. Of the increase of weight above-mentioned, it was found that about one-third, or one-fourth (for the proportion varied from causes that I could not discover), was due to the condensation of air, the rest was due to moisture. The oxide I employed was perfectly pure, and prepared by exposing metallic copper to heat. Dr. Ure states, 'that 100 grains of the oxide prepared from the nitrate of copper exposed to a red heat merely till the vapours of nitric acid were expelled, absorbed in the ordinary state of the atmosphere from .1 to .2 grain in the space of an hour or two, and about half that quantity in a very few minutes.'

In determining the quantity of water formed by the oxide of copper in the usual manner, there is yet another difficulty to contend with, to which we have alluded above, and which we shall here briefly notice. It has been stated, that complete combustion seldom or never takes place during one exposure to heat, and that in many cases the oxide ought to be removed from the tube and retritured. Now it was found, almost invariably, that during the second exposure to heat, the tube, instead of *losing* additional weight, actually became *heavier*, sometimes to the amount of .03 grain, though often much less than this. I was a good deal puzzled to account for this anomaly at first, but believe that it arose chiefly from the reoxydation of the partially-reduced oxide, by the air of the atmosphere."

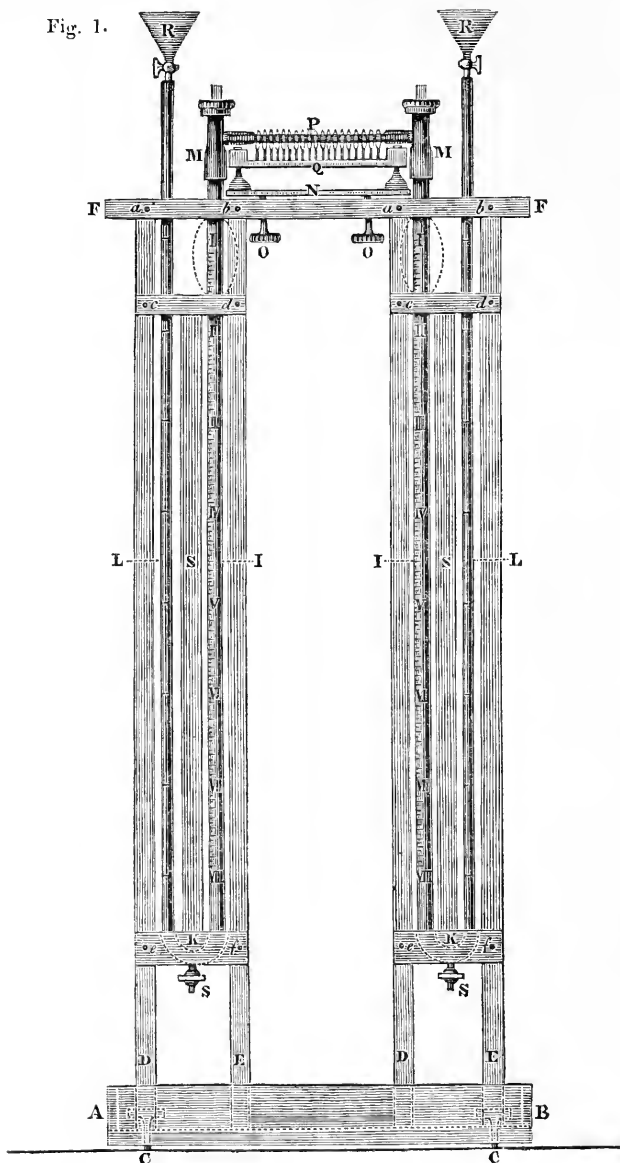
its bulk) : or, 2. The original bulk of the oxygen may be *increased*, in which case the oxygen must exist in the substance in a *greater* proportion than it exists in water ; or, 3. The original bulk of the oxygen gas may be *diminished*, in which case the *hydrogen must predominate*.

Hence it is obvious, that in the first of these cases the composition of a substance may be determined by simply ascertaining the quantity of carbonic acid gas yielded by a known quantity of it ; while in the other two, the same can be readily ascertained by means of the same data, and by noting the excess or diminution of the original bulk of the oxygen gas employed. Such are the simple and universally admitted principles on which the following method of analysis is founded ; the only novelty in which, therefore, is the form of the apparatus ; and of this the following summary sketch, and annexed figures, will convey every requisite information.

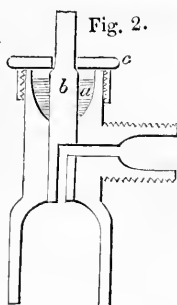
“ Fig. 1. represents a front view or elevation of the whole apparatus in the act of being employed. A B is a platform, two feet square, surrounded by a ledge about two inches and a half high, for preserving any mercury that may chance to fall about, and furnished with four adjusting screws (of two of which, c c are sectional views), by means of which it may be placed perfectly horizontal. Into this platform, in the manner represented, are fixed perpendicularly four square pillars, D E, D E, about four feet and a half high, at the top of which is placed another small platform, F F, about four inches wide, and which may be fixed or removed at pleasure by means of the brass pins a b, a b. I I are glass tubes graduated with the utmost care to hundredths of a cubic inch, and which are cemented at bottom into semicircular iron tubes enclosed in the blocks K K (as represented by the dotted lines). These iron tubes project a little below the wood at the lower part, where they are furnished with iron stop-cocks, s s, for drawing off the mercury when it may be necessary. Into the other end of these semicircular tubes are likewise cemented the glass tubes L L (of smaller dimensions, and a little longer than the tubes I I), and forming with them, when taken together, inverted syphons. The smaller tubes, L L, are represented as surmounted by funnels, R R, furnished with stop-cocks, the

object of which is to permit the mercury to flow into them with any velocity that may be required. On the tops of the

Fig. 1.

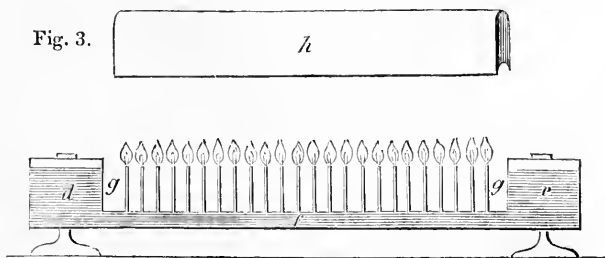


larger tubes, *1 1*, are cemented the vertical stop-cocks *MM*, of which fig. 2 is a sectional view on a larger scale, and which renders the construction so obvious, that perhaps no further remark is necessary, than merely stating that the cup *a* is filled with oil, and that the plug, *b*, which is square at the upper part, and adapted to a key, is furnished with a shoulder, on which the screw-cap, *c*, rests, and by means of which it may be tightened at pleasure*.



“ On the platform, *FF* (fig. 1.), is a thin piece of wood, capable of being raised or depressed at pleasure, by means of the screws, *oo*; on this the lamp *Q* is placed, which may thus be placed at any distance that may be required from the tube *P*. Fig. 3, is an enlarged view of this lamp; it consists of two

Fig. 3.



reservoirs, *d e*, for holding the spirit, connected together by means of the tube, *f*, into which are placed, at the distance from one another of about $\frac{1}{3}$ of an inch, a number of vertical burners, *g g*, &c., about $\frac{1}{12}$ of an inch in diameter, and $\frac{3}{4}$ of an inch long, and *made as thin* as possible, with the view of preventing the conduction of the heat. These burners are each furnished with a few threads of cotton, and are bent a little alternately like the teeth of a saw, in order that their flame

* “ The syphons are fixed together independently of the general framework, and may be removed at pleasure by taking out the pins *cd*, *cd*, and *ef*, *ef*. This admits of their being replaced by others of different sizes. Those of a larger size have balls near the top, as represented by the dotted lines, and may contain as much as 20 cubic inches of gas. It much facilitates the process of determining the exact quantity of gas contained in the apparatus, to have both legs of the syphon graduated, which may be easily done so as to obviate the effects of capillary attraction when the tubes are not both of the same calibre.

may envelope the tube *p*, (fig. 1.) more completely: *h* is a cover for the wick of the lamp when not in use. The tube *p*, (fig. 1.) is of green or bottle glass, moderately stout, and about $\frac{1}{2}$ of an inch internal diameter. It is fixed between the horizontal parts of the vertical cocks, *mm*, so as to be perfectly air-tight; and when required, the whole, or any part of it, may be heated by means of the lamp *q*, at the pleasure of the operator.

“When the apparatus is to be employed, both the syphon gasometers, *IL*, *IL*, are to be filled with quicksilver, and a small green glass retort, containing the requisite quantity of chlorate of potash, (and which had been previously heated so as to completely expel the common air, and to fill it with oxygen gas), is to be attached to one of the cocks, as represented in fig. 4, by means of a caoutchouc tube. Heat is then to be applied, and any quantity of oxygen gas that may be required, introduced into the tube *i*. After the whole has acquired the temperature of the atmosphere, the exact quantity of the gas is to be accurately noticed, as well as the state of the barometer and thermometer at the same time. The tube *p*, containing the substance to be analyzed, is then to be firmly fixed between the cocks *mm**, and subjected to heat, during which the oxygen gas is to be transferred from one syphon to another, through the red-hot tube, with any velocity that may be required, and which may be regulated by means of one of the stop-cocks of the funnels, *rr*, and the stop-cock *s*, of the opposite syphon.

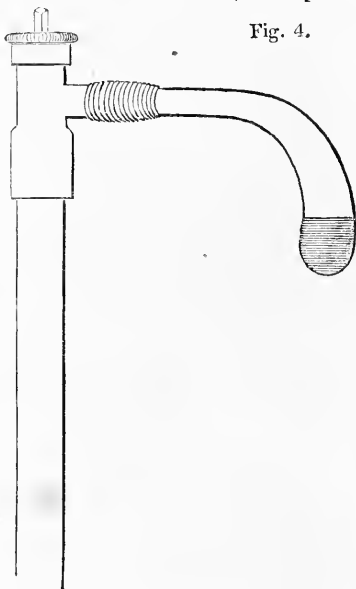


Fig. 4.

“Such is a general view of the apparatus, and the principles

* “I have tried various modes of connecting the tube so as to ensure its being air-tight. Caoutchouc answers very well; but the best substance I have hitherto employed are slips of thin moistened hogs’ bladder, tied on very tightly with fine *dry* twine. The twine is then to be moistened also, and the whole kept in this state till the end of the experiment.”

of its operation ; but perhaps a few practical remarks on some of the circumstances to be attended to during its employment, may not be deemed superfluous.

“ The substance to be analyzed may be placed in a small tray made of platina foil, and introduced alone into the tube *r*, and gradually submitted to the action of heat and oxygen gas ; but this does not answer well with organic compounds, as a portion of them is apt to escape combustion. Another method is, to mix the substance with pure silicious sand, and to retain the mixture in the centre of the tube by means of asbestos. But this method often fails, except there be about an inch of the oxide of copper at each end of the tube, which must be kept red hot during the experiment, and in this case it succeeds completely with many substances. Another method, and that which the most generally succeeds, is to mix the substance with peroxide of copper, to heat these together in the tube in the first place, and afterwards to open the other stop-cock and send the oxygen gas through the ignited and partially reduced oxide, by means of which it again becomes peroxidized ; and any portion of the substance that had escaped complete combustion in the first part of the experiment, is now completely burnt. This last method is also that employed when it is required to determine the quantity of carbonic acid gas yielded by a given quantity of any substance ; only in this case, of course, oxygen gas is not required, and the contents of the tube *r*, must be taken out and well triturated, and subjected to heat a second time. If it should be required to analyze the gas formed, one method of removing it from the tube *r* is represented at fig. 5 ; and others will readily occur to the practical chemist.

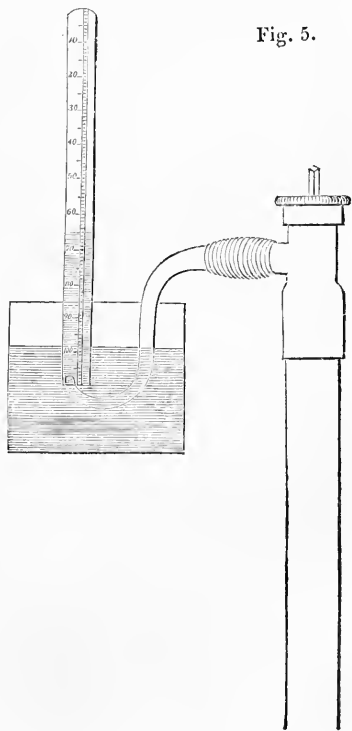


Fig. 5.

“ The following are some of the advantages of this apparatus, and mode of analyzing organic compounds. In the first and chief place, *there is nothing to be apprehended from moisture*. Whether the substance to be analyzed be naturally a hydrate, or in whatever state it may be with respect to water, the results will not be affected; and the great problem, whether the hydrogen and oxygen exist in the substance in the proportions in which they form water, or whether the hydrogen or oxygen predominates, will be equally satisfactorily solved, and that (of course within certain limits), independently of the weight of the substance operated on*. When, however, it is the object to ascertain the quantities of carbonic acid gas and water yielded by a substance, it is, of course, necessary to operate on a known weight; but this being once determined, there is no fear, as in the common methods, of exposing the substance to the atmosphere as long as may be necessary. The hygrometric properties of the oxide of copper, as well as its property of condensing air, are also completely neutralized, for the whole, at the end of the experiment, being left precisely in the same state as it was at the commencement, the same condensation of course must take place, and any little differences that may exist are rendered quite unimportant from the bulk of oxygen gas operated on, which of course should, in all instances, be considerably greater than that of the carbonic acid gas formed. Another advantage of this method is, that more perfect combustion is ensured by it than by any other that I am acquainted with. There is also no trouble of collecting or estimating the quantity of water, a part of the common process attended with much trouble, and liable to innumerable accidental errors, besides those already mentioned, and which there is no method of obviating or appreciating; here, on the contrary, the results are obtained in an obvious and permanent form, and, from the ease with which they are thus verified, comparatively very little subject to error.

* “ It is to be observed, that, throughout the experiments, great care is taken that the gases are *saturated with moisture*; the errors from this cause are thus rendered definite, and are easily corrected by tables calculated for the purpose from the most accurate data, and which will be given in a subsequent communication.

“ It need scarcely be stated, that the form and principles of this apparatus render it well adapted for many other chemical operations besides the analysis of organized substances. Such, for example, as the reduction of oxides by hydrogen, and a variety of others that will readily occur to the practical chemist.”

Having thus given in detail the account of Dr. Prout's apparatus, and his directions for using it, I shall proceed to the examination of the proximate principles of vegetables, and to some details respecting the relative proportions of their ultimate elements. In reference to this subject, the following general conclusions have been given by MM. Gay-Lussac and Thenard.

a. A vegetable substance is always acid, when the oxygen which it contains is, to the hydrogen, in a proportion greater than is necessary to form water, or where there is *excess of oxygen*.

b. A vegetable substance is resinous, oily, or alcoholic, where the oxygen is to the hydrogen in a less proportion than in water, or where there is *excess of hydrogen*.

c. A vegetable substance is neither acid nor resinous, but saccharine, mucilaginous, &c., where the oxygen and hydrogen are in the same relative proportion as in water, or where there is *no excess of either*.

To the correctness of these results, there are some exceptions which have been pointed out by M. Saussure, (Thomson's *Annals*, vol. vi.) and by Mr. Daniell, (*Journal of Science and Arts*, vol. vi. p. 326,) and which tend considerably to shake our confidence in their entire accuracy.

The following Table exhibits the results of the analysis of several substances, by the mode above described, as practised by Gay-Lussac.—Thenard's *Treatise on Chemical Analysis*, translated by A. Merrick.

SUBSTANCES ANALYZED.	Carbon contained in that body.	Oxygen contained in that body.	Hydrogen contained in that body.	Or supposing the oxygen and hydrogen to be in the state of water in the vegetable substance.		
				Carbon.	Water.	Excess of Oxygen.
Sugar . .	42.47	50.63	6.90	42.47	57.53	0
Gum arabic .	42.23	50.84	6.93	42.23	57.77	0
Starch . .	43.55	49.68	6.77	43.55	56.45	0
Sugar of milk	38.825	53.834	7.341	38.825	61.175	0
Oak . .	52.53	41.78	5.69	52.53	47.47	0
Beech .	51.45	42.73	5.82	51.45	48.55	0
Mucous acid .	33.69	62.67	3.62	36.69	30.16	36.15
Oxalic acid . .	26.57	70.69	2.74	33.57	22.87	50.56
Tartaric acid .	24.05	69.32	6.63	24.05	55.24	20.71
Citric acid . .	33.81	59.86	6.33	33.81	52.75	13.44
Acetic acid .	50.22	44.15	5.63	50.22	46.91	2.87
Resin of turpent.	75.94	13.34	10.72	75.94	15.16	Hydrogen in excess. 8.90
Copal .	76.81	10.61	12.58	76.81	12.05	11.14
Wax . .	81.79	5.54	12.67	81.79	6.30	11.91
Olive oil . .	77.21	9.43	13.36	77.21	10.71	12.08

Section III. OF THE PROXIMATE ELEMENTS OF VEGETABLES.

THE *proximate* principles of vegetables are chiefly separable from each other by the action of certain solvents, of which the principal are cold and hot water, alcohol, ether, and a few of the acids. The manner of applying these will be made more obvious by the details in the following Sections, than by any general account which could here be given of the various steps of the analysis. The number of proximate principles which are thus capable of being distinguished and separated from

each other, is considerable; those which have been most accurately examined are enumerated in the following Table, and will each form the subject of a separate Section; while those which are less perfectly known, will be adverted to under the titles of those which they most nearly resemble.

1. Gum.
2. Sugar.
3. Starch.
4. Gluten.
5. Extractive matter.
6. Lignin.
7. Tannin.
8. Colouring matter.
9. Wax.
10. Fixed oil.
11. Volatile oil.
12. Camphor.
13. Resins.
14. Bituminous substances.
15. Vegetable alkalis.
16. Vegetable acids.
 - a. Tartaric acid.
 - b. Oxalic acid.
 - c. Benzoic acid.
 - d. Citric acid.
 - e. Malic acid.
 - f. Gallic acid.

Section IV. GUM.

GUM is contained in considerable quantities in the sap of many vegetables, and frequently appears as a spontaneous exudation. *Gum arabic* may be taken as a specimen of pure gum. Its specific gravity is about 1.4 or 1.5. It has a slightly yellow tint, and is translucent, inodorous, and insipid. It dissolves in water, forming a viscid solution, or *mucilage*, from which it may be obtained nearly in its original state by evaporation; it is insoluble in alcohol, which, therefore, causes a white flaky preci-

pitate in its aqueous solution ; it is also insoluble in ether and oils ; it undergoes no change by exposure to air, and its aqueous solution does not ferment, but only becomes slightly sour when kept for a long time.

Chlorine converts gum into citric acid.

Gum is decomposed by sulphuric and nitric acids : the former produces water, acetous acid, and charcoal ; the latter, among other products, converts a portion of the gum into a white acid substance, called the *mucous acid*, and which is analogous to that obtained from sugar of milk, or *saccholactic acid*, under which head its preparation is mentioned : malic and oxalic acids are also formed.

Dilute sulphuric and muriatic acids dissolve gum without change.

The alkalis, and solutions of the alkaline earths, also dissolve gum, and the addition of acids occasions its partial precipitation without having undergone much apparent alteration. It combines with a few of the other metallic oxides. A strong solution of permuriate of iron, dropped into a concentrated mucilage, forms a brown jelly of difficult solubility. Silicated potassa also occasions a white flaky precipitate in dilute mucilage, and is, according to Dr. Thomson, a very delicate test of gum. According to Dr. Duncan, jun., however, this precipitate is produced only by solution of the lighter coloured specimens of gum, which have different properties from those of darker colour. The precipitation, when it does occur, Dr. Bostock suspects to take place only in consequence of the lime which gum contains : hence oxalic acid also produces a precipitate in solution of gum arabic. (Henry.) Acetate of lead occasions an abundant precipitate in the solution of gum. By mixing caustic ammonia with a boiling solution of gum, and then adding subnitrate of lead, Berzelius obtained a white precipitate, which he calls *gummate of lead*, composed of

Gum	61.75
Protoxide of lead	38.25
						<hr/>
						100.

If this compound be regarded as consisting of 1 proportional of gum, and 1 of oxide of lead, the number 180 might be assumed as the representative of gum, for $38.25 : 61.75 ::$

112 : 180. But if we consider it as a compound of 2 of gum and 1 of oxide, then 90 would be the equivalent of gum, and the following numbers nearly agree with its composition, as deduced from experiment :

6 proportionals of oxygen	.	$8 \times 6 = 48 = 53.34$
6 „ hydrogen		$1 \times 6 = 6 = 6.66$
6 „ carbon	.	$6 \times 6 = 36 = 40.$
		<hr/>
		90 100.

Dr. Ure (*Phil. Trans.* 1822) obtained from 100 parts of gum,

Oxygen	.	58.90
Hydrogen	.	5.85
Carbon	.	35.25
		<hr/>
		100.

And Dr. Prout, from a specimen of pure gum arabic, in its ordinary state, obtained (*Phil. Trans.* 1827)

Water	.	63.7	= {	Oxygen	.	55.92
				Hydrogen	.	7.08
Carbon	.	36.3				
		<u>100.</u>				

100 parts of the same gum exposed to a temperature between 200° and 212° for upwards of twenty hours, lost 12.4 parts. Hence its composition, thus dried, would be nearly

Water	.	58.6	= {	Oxygen	.	52.09
Carbon	.	41.4		Hydrogen	.	5.51
		<hr/>				
		100.				

results confirmed almost exactly by actual analysis. The same gum, further exposed to a temperature between 300 and 350° for six hours longer, assumed a deep brown colour, and seemed to have suffered decomposition, though it only lost in weight 2.6 per cent. more. Hence gum probably parts with the whole of the water not essential to its composition at the temperature of 212° , provided it be exposed for a sufficient time to that degree of heat.

Submitted to destructive distillation, gum affords carbonic acid and carburetted hydrogen gases, empyreumatic oil, water, and a considerable quantity of impure acetic acid, once con-

sidered as a peculiar acid, and distinguished by the term *pyromucous acid*.

There are several varieties of gum differing a little from each other. *Cherry-tree gum* and *gum tragacanth* do not readily dissolve in cold water, but in other respects their properties resemble those of gum arabic, especially in affording saccho-lactic acid by the action of nitric acid. To these varieties the generic term of *Cerasin* has been given by some chemists.

Sarcocolla appears also to be a variety of gum. Its solution, however, is precipitated by tan: it exudes in yellowish drops from the *pænea sarcocolla*, a plant native in Ethiopia.

The effects of re-agents upon the solutions of different kinds of gum have been found to vary considerably; upon this subject, much information will be found in a paper published by Dr. Bostock. (Nicholson's *Journal*, xviii. 28.)

Vegetable Jelly.—*Pectic Acid*.—When the expressed juice of certain vegetables, but especially of ripe fruits, is carefully evaporated at a temperature of 200°, the concentrated portion often concretes into a tremulous gelatinous mass; this has been long known as a substance perfectly distinct from animal jelly and from the modifications of gluten, and as containing no nitrogen; and has very generally been considered as a compound of gum and vegetable acid. The nature of this jelly has more lately been investigated by Braconnot, (*Ann. de Chim. et Phys.* xxviii. 173;) and finding that it combines with bases, and may again be separated from them by the stronger acids, he has termed it *pectic acid* (from *πηκτις*, *coagulum*). The *alkaline pectates* are soluble, but the *pectate of lime* is insoluble. He chiefly procured it from the rasped roots of carrots and turnips; it is also deposited from a mixture of one-fourth of the juice of cherries and three-fourths of the juice of gooseberries, and, when washed carefully with cold distilled water, is pure, with the exception of a little colouring matter.

To obtain jelly or pectic acid from the carrot, the root is rasped, pressed, and washed with common water, until the latter passes off limpid. Every 100 parts of the pressed carrot, with 5 parts of bicarbonate of potash, are boiled in water to form a clear fluid, and then pressed; a strong solution of pectate of potash is thus obtained, which, being decomposed by excess of muriate of lime, gives an insoluble pec-

tate of lime. This, washed, and treated with water acidulated by muriatic acid, and finally with pure water, affords pure pectic acid.

In preparing it in this or any other way, water containing earthy salts should be carefully avoided, as they are decomposed, and precipitate it. It has been much recommended in France as a part of the diet of invalids, and is said to be an antidote against many of the poisonous salts. (*Ann. de Chim. et Phys.*, xxx. 96.) I suspect, however, as Dr. Turner has remarked, "that the original account of the properties of this substance has been exaggerated, and that its claim to be regarded as an independent proximate principle has not yet been clearly established." Vauquelin ascertained that vegetable jelly, treated with excess of potassa, became converted into oxalate of potassa, a fact more recently investigated by Gay-Lussac. (See OXALIC ACID.)

Section V. SUGAR.

SUGAR may be extracted from the juice of a number of vegetables, and is contained in all those having a sweet taste: that which is commonly employed is the produce of the *arundo saccharifera*, or *sugar-cane*, a plant which thrives in hot climates. Its juice is expressed and evaporated with the addition of a small quantity of lime, until it acquires a thick consistency; it is then transferred into wooden coolers, where a portion concretes into a crystalline mass, which is drained and exported to this country under the name of *muscovado* or *raw sugar*. The remaining liquid portion is *molasses* or *treacle*.

The following is a sketch of the process by which raw sugar is purified in this country.

Raw sugar is chosen by the refiner by the sharpness and brightness of the grain, and those kinds are preferred which have a peculiar gray hue. Soft-grained yellow sugars, although they may be originally whiter, are not so fit for the purposes of the manufactory, and it is for this reason that sugars from particular countries are never used: such are those from the East Indies, Barbadoes, &c. They do not possess the property

of crystallizing so perfectly, and approach in this respect to the nature of grape sugar.

There appear to be two perfectly distinct kinds of saccharine matter: one, when pure, is transparent and colourless, and crystallizes under proper management in a regular form, generally in flattened six-sided prisms; the other is uncrySTALLIZABLE, and generally highly charged with colouring matter. This colouring matter is not, perhaps, essential to it, but may arise in the present case from the effect of fire, by the agency of which it is peculiarly prone to decomposition. We may mention, as familiar instances of these two, *white sugar-candy* and *treacle*. The juice of the cane is composed of these ingredients, and though they are in some degree separated in our Indian colonies by the process of evaporation and filtration, yet the raw sugar which we receive contains still much of the latter combined with the former. The process of refining consists in further separating the two.

The proper sugar being selected, the *pans*, which resemble in some measure those used in the West Indies, are charged with a certain portion of lime-water, with which bullocks' blood is well mixed by agitation. They are then filled with the sugar, which is suffered to stand a night to dissolve. The use of the lime-water is not, as is generally supposed, to neutralize any free acid in the raw material: but, by combining with the molasses, to render it more soluble, and thus to facilitate its separation from the pure solid sugar. In the purer kinds, and more especially when the refined is again melted over for the purpose of bringing it to its utmost degree of purity, lime is not used, the quantity of molasses being so small as to be easily removed by the agency of water alone.

Fires are lighted under the pans early in the morning, and when the liquid begins to boil, the albumen of the blood coagulates and rises to the top, bringing all the impurities of the sugar with it. These are taken off with a skimmer. The liquid is kept gently simmering and continually skimmed, till a small quantity, taken in a metallic spoon, appears perfectly transparent: this generally takes from four to five hours. The whiteness of the sugar is not at all improved by this process, but is even sometimes deteriorated from the action of the fire; it only serves to remove all foreign impurities. When the

solution is judged to be sufficiently clear, it is suffered to run off into a large cistern. The pans are then reduced to half their size by taking off their fronts, and a small quantity is returned into each. The fires are now increased, and the sugar made to boil as rapidly as possible, till a small quantity taken on the thumb is capable of being drawn into threads by the fore-finger. Nothing but practice can ascertain the exact point at which the boiling should be stopped: if it is carried too far, the molasses is again bound up with the sugar; and if it is not carried far enough, much of the sugar runs off with the molasses in the after-process. When this point is ascertained, the fire is instantly damped, and the boiling sugar carried off in basins to the *coolers*; a fresh quantity is then pumped into the pans, which is evaporated in the like manner.

When the sugar is in the coolers, it is violently agitated with wooden oars till it appears thick and granulated, and a portion taken on the finger is no longer capable of being drawn into threads. It is upon this agitation in the cooler that the whiteness and fineness of grain in the refined sugar depend. The crystals are thus broken whilst forming, and by this means the whole is converted into a granular mass, which permits the coloured liquid saccharine matter to run off, and which would be combined with the solid if suffered to form in larger crystals. This granular texture likewise facilitates the percolation of water through the loaves in the after-process, which washes the minutely-divided crystals from all remaining tinge of the molasses. That this is the true theory of the whitening of sugar by the process of refining, appears from a comparison with the process of making candy. In this latter, the raw material is cleared and boiled exactly in the same manner; but instead of being put into coolers and agitated, it is poured into pots, across which threads are strung, to which the crystals attach themselves; these are set in a stove, and great care is taken not to disturb the liquid, as upon this depends the largeness and beauty of the candy. In this state it is left for five or six days, exposed to a heat of about 95° , when it is taken out and washed with lime-water: this takes off the molasses from the outside, but a great quantity is combined in the crystals, and the consequence is, that candy is never whiter than the sugar from which it is made.

When the sugar has arrived at that granular state in the coolers above described, it is poured into conical earthen moulds, which have previously been soaked a night in water. In these it is again agitated with sticks, for the purpose of extricating the air-bubbles which would otherwise adhere to the sugar and the moulds, and leave the coat of the loaf rough and uneven. When sufficiently cold, the loaves are raised up to some of the upper floors of the manufactory, and the paper stops being removed from their points, they are set, with their broad ends upward, upon earthen pots. The first portions of the liquid molasses soon run down, and leave the sugar much whitened by the separation. This self-clearance is much assisted by a high temperature; and when it is perfected, pipe-clay, carefully mixed up with water to the consistence of thick cream, is put upon the loaves to the thickness of about an inch: the water from this slowly percolates the loaves; and, washing the solid sugar from all remains and tinge of the molasses, runs into the pots. The clay is of no other use than to retain the water, and prevent its running too rapidly through the mass, by which too much of the sugar would be dissolved: a sponge, dipped into water, acts in the same manner. The process of *claying* is repeated four or five times, according to the nature of the sugar, and the degree to which it has been boiled. When the loaves are perfectly cleansed from all remains of the coloured fluid, they are suffered to remain some time for the water to drain off; when this is completed, they are set, with their faces down, when all remains of it return from their points, and it is equally diffused throughout: they are then set in a stove, heated to about 95° , and thoroughly dried.

The syrup, or the mixed solution of sugar and molasses which runs into the pots, is mingled in the next boilings with the solution of raw sugar in the pans, and again evaporated. It is divided according to its fineness; the first running, containing, of course, more molasses, is reserved for the coarser loaves; whilst the last, being little else than a solution of sugar, is boiled into loaves, of the same degree of fineness as those from which it ran. The lowest syrups are boiled into what is called *bastard sugar*, from which the molasses runs with very little mixture of the solid sugar. This is called *treacle*, and is totally incapable of further crystallization.

The produce of 1 cwt. of raw sugar worked in this manner is, upon an average,

lbs.
63 refined
18 bastard
27 molasses
4 lost weight, dirt, &c.

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The process above described may almost be considered as mechanical. The only truly chemical parts of it are the clearing with blood, and the use of lime-water, which, leaving the solid sugar untouched, combines with the molasses, and rendering it in some measure saponaceous, facilitates its solution during the percolation of the water.

Attempts have lately been made to whiten the sugar during its boiling, by the addition of charcoal. This destroys some of the colouring matter of the molasses, and tends materially to whiten the sugar, especially if the charcoal employed be partly of animal origin.

Another attempt has been made to improve the process of claying, by the substitution of a strong solution of very white sugar for the clay. The idea was, that the water having a stronger affinity for the molasses than for the solid sugar, would, in its passage through the loaves, wash away the former, and leave the latter in its place, and that more weight and a closer grain would thus be obtained. The idea was ingenious, but the advantages scarcely counterbalanced the additional expense of preparing the solution of fine sugar in the first instance. This plan has, in Mr. Howard's patent, been combined with a mode of evaporating *in vacuo*, or, at least, under a greatly diminished atmospheric pressure, by which exposure to any temperature liable to injure the sugar is effectually prevented.

According to Dr. Henry, "a mixture of one part of water and three of sugar boils rapidly at 230° ; and from this to 240° is its due temperature. If a solution of sugar be further concentrated by the evaporation of water, the thermometer rises to 340° . The sugar then begins to turn black, and at 370° it takes fire, on applying flame to its vapour, and burns strongly, leaving a residuum of charcoal."

Sugar may be obtained from the sap of many other plants. It exists in large quantity in the sugar maple (*acer saccharinum*) and in the root of the common beet (*beta vulgaris*). The manufacture of sugar from beet-root has been successfully and extensively pursued in France: many interesting details respecting it will be found in a paper in the *Quarterly Journal*, xxi. 252. The roots, having been softened in water, are sliced, and the juice is expressed and boiled down to about two-thirds its bulk with the addition of a little lime; it is then strained, again evaporated, and purified in the same way as cane sugar. 100lbs. of the root furnish between 4 and 5lbs. of purified white sugar, besides a quantity of syrup, at the average expense of between threepence and fourpence a pound.

A peculiar variety of sugar has been extracted from the roots of liquorice, but it is not economically applicable.

In many ripe fruits sugar is a predominating ingredient; and in dried grapes, figs, &c., it is often seen as a superficial incrustation. Though these kinds of sugar differ a little from each other, they can scarcely be regarded as distinct species.

Honey is also a variety of sugar containing a crystallizable and an uncrystallizable portion, the predominance of one or other of which gives to it its peculiar character; they may be partially separated by mixing the honey with alcohol, and pressing it in a linen bag; the liquid sugar being the most soluble, passes through, leaving a granular mass, which forms crystals, when its solution in boiling alcohol is set aside. Honey also frequently contains wax, and a little acid matter.

Sugar is a white brittle substance of a pure sweet taste, soluble in its own weight of water at 60°. Its specific gravity is about 1.5. Boiling water dissolves a considerably larger quantity. This solution is called *syrup*; it is viscid, and furnishes crystals in the form of four and six-sided prisms, irregularly terminated, composed, according to Berzelius, of 100 sugar + 5.6 water. Sugar is soluble in alcohol, but more sparingly so than in water. It takes up about one-fourth its weight of pure white sugar.

Nitric and sulphuric acids decompose sugar; the former converts it into oxalic acid; the latter evolves charcoal and produces water and acetous acid. It is a striking experiment to mix about equal weights of syrup and sulphuric acid; the

mixture, when stirred, presently becomes brown and black, then suddenly heats, and passes into the state of an almost solid magma of charcoal: the acid appears suddenly to abstract from the sugar the elements of water.

The alkalis dissolve sugar, and destroy its sweet taste, which re-appears if an acid be added. When, however, the alkalis are left for a long time in the contact of sugar they effect a more important change, becoming carbonated, and converting the sugar into gum. From a solution of sugar in lime-water, Mr. Daniell, who has obligingly furnished me with the principal materials of this section, obtained crystals of carbonate of lime and a portion of gum. The addition of phosphuret of lime to syrup produces an analogous change.—*Journal of Science and the Arts*, vol. vi. p. 32.

When protoxide of lead is digested with sugar and water, a portion is dissolved and afterwards separates in the form of a white insipid powder (*saccharate of lead*), insoluble in water, and composed, according to Berzelius, of

Sugar	41.74
Oxide of lead	58.26
						<hr/>
						100.00

When sugar is exposed to a heat of 212° , it undergoes no other change than that occasioned by the loss of adhering water; but at 300° it begins to fuse, becomes brown, evolves a little water, and is resolved at higher temperatures into new arrangements of its component elements. Dr. Prout found that sugar, exposed for seven hours to a temperature of 300° , only lost 0.6 *per cent.* of its weight, but its properties were permanently injured. If suddenly elevated to a temperature of about 500° , it bursts into flame.

The relative proportions of elements in gum and sugar appear, from the experiments of Gay-Lussac (page 424), to be nearly the same. The analyses of these two substances by Berzelius afforded slight differences only; according to him they contain,

Carbon	.	.	.	41.906	} = 100 gum.
Oxygen	.	.	.	51.30 6	
Hydrogen	.	.	.	6.788	
Carbon	.	.	.	44.200	} = 100 sugar.
Oxygen	.	.	.	49.015	
Hydrogen	.	.	.	6.785	

The equivalent of sugar, deduced from the analysis of the compound with oxide of lead, provided we regard that compound as containing 1 proportional of each of its components, is 82, a number reconcileable with the ultimate of analysis of Berzelius, who regards sugar as composed of

6	proportionals of carbon (6×6)	.	.	.	=	36
5	„ oxygen (8×5)	.	.	.	=	40
5	„ hydrogen (1×5)	.	.	.	=	5
						<hr/> 81

According to Dr. Prout (*Phil. Trans.* 1827), the most perfect sugar is sugar-candy carefully prepared from cane sugar: this, purified, by repeated crystallizations from water and alcohol, and deprived of hygrometric moisture by exposure for some time to a temperature of 212° , was found to be composed of

Water	57.15
Carbon	42.85
							<hr/> 100.

All the finest and purest specimens of loaf-sugar gave precisely the same results, and may, therefore, be considered as identical in their composition with sugar-candy. The weakest or lowest of the well-defined sugars is that of honey, which consisted of

Water	63.63
Carbon	36.36

In its ordinary state, Dr. Prout observes, that this sugar usually contains more water than indicated by this analysis; that is to say, generally about 64.7 *per cent.* On the other hand, on exposure to a temperature considerably below that of boiling water, it rapidly loses about 3 *per cent.* of water, and begins to assume the fluid form; kept at the temperature of boiling water for 30 hours, it lost in one experiment upwards of 10 *per cent.* of its original weight, became of a deep brown colour, and seemed to be partially decomposed.

Sugar prepared from *starch* also belongs to this variety, as is sufficiently indicated both by its sensible properties and composition. So does *diabetic sugar*, and probably also of the *sugar of grapes, figs, &c.* When pure, all these varieties are

white, crystallize in spherules, and are permanent under the ordinary circumstances of the atmosphere.

To show that between these two extremes, sugars occur of almost every grade, Prout has given the following table of analytical results :—

	Carbon.	Water.
Pure sugar-candy . . .	42.85 . . .	57.15
*Impure sugar-candy . .	41.5 to 42.5 . .	58.5 to 57.5
East India sugar-candy (v)	41.9 . . .	58.1
English refined sugar . .	41.5 to 42.5 . .	58.5 to 57.5
East India refined sugar (v)	42.2 . . .	57.8
Maple sugar (v) . . .	42.1 . . .	57.9
Beet-root sugar (v) . . .	42.1 . . .	57.9
East India moist sugar (v)	40.88 . . .	59.12
Sugar of diabetic urine . .	36 to 40 ? . .	64 to 60 ?
Sugar of Narbonne honey	36.36 . . .	63.63
Sugar from starch . . .	36.2 . . .	63.8

On these he makes the following remarks:—"The *sugar-candies* of the shops frequently contain minute quantities of foreign fixed bodies, such as lime, &c., as well as others of a destructible character. Both the specimens of *India sugar-candy* I examined were obviously impure to the eye, being of a brown colour, and deliquescent; they contained, among other things, traces of potash. The *East India refined sugar* was perfectly white, but rather soft and friable, and it did not possess the fine and brilliant grain of the best refined sugars of commerce. For a specimen of the *maple sugar* I was indebted to Mr. Faraday; this, when I received it, was very impure and deliquescent, but by treating it by the process above alluded to, a portion was separated that differed but little in its appearance from cane sugar. The *beet-root sugar* was made and refined in France; it was perfectly white, but rather soft and fine in the grain. The *East India moist sugar* was of a very low kind, and known in commerce by the name of *Burdwan sugar*; it was deprived of its hygrometric moisture before analysis by exposure to sulphuric acid under a receiver. The *diabetic sugar* was prepared as above; the results given were obtained many years ago, and I have had no opportunity of repeating the analysis with the present apparatus; I believe,

* In these results *fixed* bodies only have been allowed for, and those marked (v), as occurring in commerce, are probably subject to slight variations in their composition.

however, that diabetic sugars in general belong to the honey variety. The *sugar of starch* was prepared by myself in the usual manner."

Manna is an exudation from the *Fraxinus Ornus*, a species of ash, growing in Sicily and Calabria. It has a sweet and somewhat nauseous taste, and is used in medicine as a mild aperient. It is very soluble in water, and more soluble in alcohol than cane sugar; the latter solution deposits it in the form of a white spongy mass. Digested in nitric acid, it yields both oxalic and saccharic acids. Its solution in water does not appear susceptible of vinous fermentation. According to Prout, manna sugar is decomposed by a temperature very little exceeding 212° . Dried at that heat it consisted of

Water	61.3
Carbon	38.7
							<hr/>
							100.

Section VI. STARCH.

STARCH, or *Fecula*, may be separated from a variety of vegetable substances; it is contained in the esculent grains, and in many roots. The process for obtaining it consists in diffusing the powdered grain or the rasped root in cold water, which becomes white and turbid; the grosser parts may be separated by a strainer, and the liquor which passes deposits the starch, which is to be washed in cold water, and dried in a gentle heat.

The common process for obtaining the starch of wheat consists in steeping the grain in water till it becomes soft; it is then put into coarse linen bags, which are pressed in vats of water: a milky juice exudes, and the starch falls to the bottom of the vat. The supernatant liquor undergoes a slight fermentation, and a portion of alcohol and a little vinegar is formed, which dissolves some impurities in the deposited starch; it is then collected, washed, and dried in a moderate heat, during which it splits into the columnar fragments which

we meet with in commerce, and which are generally rendered slightly blue by a little smalt.

Pure starch is a white substance, insoluble in cold water, but readily soluble at a temperature between 160° and 180° . Its solution is gelatinous, becomes mouldy and sour by exposure to air, and by careful evaporation yields a substance resembling gum in appearance, which is a compound of starch and water. Starch is insoluble in alcohol and in ether, and occasions no precipitate in the greater number of metallic solutions; in solution of subacetate of lead, however, it occasions a copious precipitate. The most characteristic property of starch is that of forming a blue compound with iodine; it may be obtained by adding an aqueous solution of iodine to a dilute solution of starch.

Sulphuric acid dissolves starch, and slowly decomposes it, and resolves it into new compounds, with a copious separation of charcoal. Dilute sulphuric acid does not dissolve it.

Concentrated nitric acid dissolves it at common temperatures; and when the mixture is heated, the acid and starch are decomposed, and oxalic acid is formed. Diluted nitric acid dissolves it without decomposition, forming a greenish solution, which deposits starch upon the addition of alcohol. It is slowly soluble in muriatic acid, and insoluble in acetic acid.

Potassa, triturated with starch, forms a compound which is soluble in water and in alcohol. It is decomposed, and starch separated, by acids.

Infusion of galls occasions a precipitate in the solutions of starch, which redissolves by heating the liquid to 120° , and again falls as it cools. This property Dr. Thomson considers as characteristic of starch.

By digesting subnitrate of lead in a boiling solution of starch, Berzelius obtained an insoluble compound, which he has termed *amylate of lead*, consisting of

$$\begin{array}{r} 72 \text{ starch,} \\ 28 \text{ protoxide of lead.} \\ \hline 100 \end{array}$$

It appears, by a reference to the ultimate elements of starch and sugar, that they differ little in composition, and it is there-

fore not surprising that the former is easily convertible into the latter.

The change of starch into sugar is always observed during the germination of seeds, and in the process of *malting* a similar conversion is effected.

Malt is barley which has been made to germinate to a certain extent, after which the process is stopped by heat. The barley is steeped in cold water, and is then made into a heap, or *couch*, upon the maltfloor: here it absorbs oxygen and evolves carbonic acid; its temperature augments, and then it is occasionally turned, to prevent its becoming too warm. In this process the radicle lengthens, and the plume, called by the maltsters *acrospire*, elongates; and when it has nearly reached the opposite extremity of the seed, its further growth is arrested by drying at a temperature slowly elevated to 150° or more. The malt is then cleansed of the rootlets.

According to Dr. Thomson, barley loses about 8 *per cent.* by converting it into malt, of which

1.5 is carried off by the steep-water,
3.0 dissipated on the floor,
3.0 roots separated by cleansing,
0.5 waste.

8.0

The following are his comparative analyses of unmalted and malted barley, showing the changes which have taken place in the operation.

Gum	5	14
Sugar	4	16
Gluten	3	1
Starch	88	69
					<hr/>	<hr/>
					100 barley					100 malt.

According to Prout (*Ann. de Chim. et Phys.*, v. 337), barley also contains a peculiar substance, insoluble in hot water, which he calls *hordein*, and which, during malting, is diminished in quantity and converted into sugar or starch. Hitherto hordein appears to have been confounded with starch. The following are his comparative analyses:—

	In 100 of Barley.	In 100 of Malt.
Resin	1	1
Gum	4	15
Sugar	5	15
Gluten	3	1
Starch	32	56
Hordein	55	12
	<hr/> 100	<hr/> 100

The starch of malt differs in some of its properties from that of barley.

An artificial mode of converting starch into sugar was discovered by M. Kirchoff; it consists in boiling it with very dilute sulphuric acid. A pound of starch may be digested in six or eight pints of distilled water, rendered slightly acid by two or three drachms of sulphuric acid. The mixture should be simmered for a few days, fresh portions of water being occasionally added to compensate for the loss by evaporation. After this process, the acid is saturated by a proper proportion of chalk, and the mixture filtered and evaporated to the consistence of syrup; its taste is sweet, and, by purification in the usual way, it affords a granular sugar. Dr. Tuthill digested a pound and a half of potato starch (obtained from about 9 pounds of potatoes) in a mixture of 6 pints of distilled water, and a quarter of an ounce (by weight) of sulphuric acid at a boiling heat; the mixture was afterwards stirred, and fresh water occasionally added to supply loss by evaporation. After thirty-four hours an ounce of powdered charcoal was added, and the boiling resumed for two hours. The acid was then carefully saturated by lime, and the boiling continued for half an hour, when the liquor was strained through calico. The insoluble residue, after having been washed and dried, consisted of charcoal and sulphate of lime. The filtered liquor was evaporated to the thickness of syrup; and being set aside, became, in eight days, a crystallized mass, resembling brown sugar and treacle. The sugar weighed one pound and a quarter. One pound of it, fermented in the usual way, afforded, on distillation, 14 drachms of proof spirit. (*Nicholson's Journal*, xxxiii.) MM. de la Rive and Saussure have shown that the contact of air is unnecessary in the above process; that no part of the acid is decomposed, no gas evolved, and that the actual sugar obtained exceeds, by about one-tenth, the original weight of the starch.

M. de Saussure, therefore, concludes that the conversion of starch into sugar depends upon the solidification of water, a conclusion strengthened by the following comparative analysis.—THOMSON'S *Annals*, vol. ii.

	100 Parts of Starch contain	100 Parts of Starch Sugar contain
Carbon	45.39	37.29
Oxygen	48.31	55.87
Hydrogen	5.90	6.84
Nitrogen	0.40	0.00
	<hr/> 100.00	<hr/> 100.00

This analysis of starch is somewhat at variance with that given by Gay-Lussac; indeed the small portion of nitrogen cannot be considered as an essential component. Berzelius has given the following as the component parts of starch.—THOMSON'S *Annals*, vol. v.

Carbon	43.481
Oxygen	48.455
Hydrogen	7.064
	<hr/> 100.000

If we regard the amylate of lead as consisting of 2 proportionals of starch, and 1 of oxide of lead, the number 144 will be the equivalent of starch; but this number cannot be assimilated with the theory of definite proportionals as applied to the elements of starch.

Gay-Lussac and Thenard found 43.55 *per cent.* of carbon in starch, and Dr. Ure only obtained 38.55, differences explained by the following observations of Dr. Prout.

“A very fine specimen of wheat starch, which had been prepared without the addition of the colouring matter commonly added to the starch of commerce, and which had been kept in a dry situation for many months, was found, in the ordinary columnar form in which it usually occurs, (abstracting foreign matters) to consist of

Carbon	37.5
Water	62.5

“One hundred parts of the same specimen reduced to a state of fine powder, and subjected to a temperature between 200° and 212°, for the space of twenty hours*, lost, in a mean of

“* I have reason to believe, from other experiments, that six or eight hours, or even less, of steady exposure to the boiling temperature, will sometimes reduce both starch and arrow-root, and even gum, to this state of desiccation.”

two experiments, 12.5 parts, and on being analyzed in this state, gave

Carbon	42.8
Water	57.2

which very nearly coincides with what, by calculation, it ought to have given, on the supposition that the loss of weight was owing to the escape of water, a circumstance indeed of which there could have been little doubt. Starch, however, in this state still retains water, a portion of which may be separated by subjecting it to higher temperatures. Thus, after having been exposed as above for twenty-four hours to the temperature of 212° , on being further submitted to a temperature between 300° and 350° for six hours longer, it lost 2.3 *per cent.* more, and analyzed in this state gave very nearly

Carbon	44
Water	56

It had now acquired a slight yellow colour, and seemed to have suffered some change in its properties; hence, this is probably nearly the utmost quantity of water that starch is capable of parting with, short of decomposition."

When starch is exposed to a temperature between 600° and 700° it swells, and exhales a peculiar smell; it becomes of a brown colour, and in that state is employed by calico-printers under the name of *British gum*. It is soluble in cold water, and does not form a blue compound with iodine, similar to that with unaltered starch; but the solution becomes purple, and this colour is permanently destroyed by acids. (CAVENTOU, *Ann. de Chim. et Phys.* xxxi.)

The following is F. Marcet's comparative analysis of ordinary and torrefied starch:—

	Carbon.	Oxygen.	Hydrogen.
Dry starch	43.7	49.7	6.6
Torrefied starch	35.7	58.1	6.2

Vauquelin found it to differ from gum in affording oxalic instead of mucous acid, when treated with nitric acid.

The following are the principal varieties of starch:—

i. *Arrow-root*, the fecula of the *Marantha Arundinacea*.

This species of starch has been examined by Dr. Prout; (*Phil. Trans.*, 1827;) he found it to consist of

Carbon	36.4
Water	63.6

One hundred parts of arrow-root, exposed for twenty hours to a temperature between 200° and 212° , lost fifteen parts. Hence its composition, when thus dried, was very nearly the same as that of wheat starch similarly exsiccated; or it consisted of

Carbon	42.8
Water	57.2

On being subjected to the full temperature of 212° for six hours longer it lost 3.2 *per cent.* more, and was then reduced to a state similar to that of starch dried between 300° and 350° , or it consisted very nearly of

Carbon	44.4
Water	55.6

“ When subjected to the temperature of 300° and 350° for six hours longer, it lost 1.38 *per cent.* more of its weight, but became of a deeper yellow colour than starch similarly exposed, and consequently shewed greater marks of decomposition. Hence, this form of the amylaceous principle, like the sugar of honey before-mentioned, seems to part with the whole of the water not essential to its composition at the temperature of 212° , or even perhaps below this point if exposed for a period sufficiently long.”

ii. *Potato Starch*, obtained by reducing potato to a pulp, and washing it with cold water upon a sieve; the fecula is deposited in the form of a fine white powder, heavier than common starch, but possessed of its essential characters. According to Dr. Pearson (*Repertory of Arts*, iii. 383), 100 parts of fresh potato, deprived of skin, contain

Water	68	to	72
Meal	32	”	28
	<hr/> 100		<hr/> 100

The meal consists of

Starch	15	to	17
Fibrous matter	8	”	9
Mucilage	5	”	6
	<hr/> 28		<hr/> 32

Lampadius has also analyzed several varieties of the potato. (THOMSON'S *Annals*, v. 39.)

iii. *Sago*, extracted from the pith of several species of palm, growing in the East India islands, especially the *Cycas Circinalis*. The pith is mixed with cold water, and the starchy deposit is granulated and dried : its colour depends upon the heat at which it has been desiccated. Though it possesses the leading character of starch, that of precipitating iodine blue, it differs from common starch by its solubility in cold water. (CAVENTOU.)

iv. *Tapioca* and *Cassava* are prepared from an American plant, the *Iatropa Manihot*, the milky juice of which is poisonous, but diffused through water deposits a harmless starch, nearly allied to sago.

v. *Salop*, obtained from the roots of several species of *Orchis*, especially the *Orchis Masculata*. It differs from starch in containing a gummy matter, analogous to bassorine. (CAVENTOU, *Ann. de Chim. et Phys.* xxxi.)

Dr. Prout, referring to the identity in composition between the sugar of honey and arrow-root under the ordinary circumstances of the atmosphere, infers that differences exist among the varieties of amylaceous principles analogous to those existing among sugars ; or, in other words, that there are *low* starches as well as *low* sugars ; wheat starch he places at the head of the starches, and considers arrow-root as the lowest variety. " Whether arrow-root," he observes, " be the lowest that exists, I am unable to say ; but I have met with none lower ; and have reason to believe that the greater portion of the other varieties of the amylaceous principle known to exist, like the varieties of sugars above given, are intermediate in their composition between arrow-root and wheat starch.

" The identity of composition between wheat starch and cane sugar, and between the sugar of honey and arrow-root, seems to show that, though these bodies are not actually capable of assuming the crystalline form, yet that the original tendency among their essential elements to combine in certain proportions (and perhaps to assume certain forms) still continues to operate, though in a mitigated degree, and thus to exert, as it were, a feeble *nisus*, or endeavour toward the maintenance of certain definite modes of existence."

In reference to what are usually called the extraneous or foreign ingredients of certain vegetable principles, Dr. Prout has the following remarks:—

“ It has been known from the very infancy of chemistry, that all organized bodies, besides the elements of which they are essentially composed, contain minute quantities of different foreign bodies, such as the earthy and alkaline salts, iron, &c. These have been usually considered as mere mechanical mixtures accidentally present ; but I can by no means subscribe to this opinion. Indeed, much attention to this subject for many years past has satisfied me that they perform the most important functions ; in short, that organization cannot take place without them. This point will be more fully investigated hereafter : at present it is sufficient merely to observe, that many of those remarkable changes which crystallized bodies undergo on becoming organized, are more apparent than real ; that is to say, their chemical composition frequently remains essentially the same ; and the only point of difference that can be traced, is the presence of a little more or less of water, or the intimate mixture of a minute portion of some foreign fixed body. There is no term at present employed which expresses this condition of bodies, and hence, to avoid circumlocution, I have provisionally adopted the term *merorganized*, (*μέρος pars vel partim*) meaning to imply by it that bodies on passing into this state become partly, or, to a certain extent, organized. Thus starch I consider as *merorganized* sugar, the two substances having, as we shall see presently, the same essential composition, but the starch differing from the sugar by containing minute portions of other matters, which, we may presume, prevent its constituent particles from arranging themselves in the crystalline form, and thus cause it to assume totally different sensible properties.”

Section VII. GLUTEN.

GLUTEN may be obtained from wheat-flour, by forming it into a paste and washing it under a small stream of water. The starch is thus gradually washed away, and a tough elastic insoluble substance remains, which is gluten.

Its colour is grey, and, when dried, it becomes brown and brittle. It is nearly insoluble in water and in ether. When allowed to putrefy, it exhales an offensive odour, and when submitted to destructive distillation it furnishes ammonia, a circumstance in which it resembles animal products. Most of the acids and the alkalis dissolve it.

Acted upon by alcohol, a portion of gluten is dissolved, and the solution, after having remained to deposit a little extraneous matter, affords, on evaporation, a peculiar substance of a yellowish colour, brittle, and having a balsamic taste. The undissolved portion of the gluten forms soapy compounds with the alkalis, and, instead of fermenting like the original gluten, exhales the odour of putrid urine. Hence it appears that, by the action of alcohol, gluten is separated into two principles, the one soluble and the other insoluble in that menstruum. M. Taddei, the author of these researches, calls the former *Gliadine*, from γλιν, gluten, and the latter *Zimoma*, from ζυμη, a ferment.—*Giornale di Fisica*, ii. p. 360. Berzelius does not admit these as distinct principles, but regards the alcohol as separating what is termed the gluten of wheat into a portion soluble in alcohol, which is real gluten, and into an insoluble portion, which is vegetable *albumen*. The alcoholic solution, when evaporated, deposits the gluten in viscid flakes.

When gluten is digested with water, the solution precipitates by muriate of tin and by the acetate of lead. It dissolves in acetic acid, and is precipitated by the alkalis, by ferrocyanate of potassa, perchloride of mercury, tincture of galls, and tannin. According to Taddei, wheat-flour, which contains a due proportion of sound gluten, produces a fine blue colour when kneaded with powdered guaiacum, but that colour is not pro-

duced by spoiled grain, or that which is deficient in gluten. (*Quarterly Journal*, vii. 377.)

Gluten is an essential ingredient in wheat-flour; it contributes much to its nutritive quality, and gives considerable tenacity to its paste.

A substance, much resembling the insoluble part of gluten, has been found in the juices of other vegetables, especially in those which are milky and coagulable by acids. It is contained in the sap of the houseleek, of the cabbage, and of most of the cruciform plants. Submitted to destructive distillation, it affords ammonia, and is in other respects similar to the animal principle, called albumen: hence it has been termed *vegetable albumen*.

The principles which have now been adverted to, viz., sugar, starch, gum or mucilage, albumen, and gluten, constitute the principal nutritive ingredients in most of the esculent vegetables. Wheat grown in this country contains from 18 to 24 *per cent.* of gluten, the remainder being principally starch. The wheat of the south of Europe generally contains a larger quantity of gluten, and is therefore more excellent for the manufacture of macaroni, vermicelli, and other preparations requiring a glutinous paste. The excess of gluten in wheat-flour, compared with other grain, renders it peculiarly fit for making bread; for the carbonic acid, extricated during the fermentation of the paste, is retained in consequence of its adhesiveness, and forms a spongy and light loaf.

A hundred parts of barley contain upon an average 80 parts of starch, 6 of gluten, and 7 of sugar, the remaining 7 parts being husk.

From 100 parts of rye Sir Humphry Davy obtained 61 parts of starch and 5 of gluten.

From 100 parts of oats he procured 59 of starch, 6 of gluten, and 2 of sugar.

100 parts of pease afforded about 50 of starch, 3 of sugar, 4 of gluten, and a small portion of extractive matter.

100 parts of potato yield, upon an average, 20 parts of starch; they may be considered in general as containing from one-fourth to one-fifth their weight of nutritive matter.

The turnip, carrot, and parsnip, chiefly contain sugar and mucilage; 1000 parts of common turnips give about 34 of

sugar, and 7 of mucilage; 1000 parts of carrots furnish about 95 of sugar, and 3 of mucilage; and the same quantity of parsnips afford 90 of sugar and 9 of mucilage. The loss of weight in the above cases is referable to water, and inert vegetable matter possessed of the properties of woody fibre.

The following Table, drawn up by Sir H. Davy, exhibits the relative proportions of soluble and of nutritive matter contained in 1000 parts of the different vegetable substances enumerated in the first column (*Agricultural Chemistry*, 4to., p. 131):—

VEGETABLES or VEGETABLE SUBSTANCES.	Whole quantity of Soluble or Nutritive Matter.	Mucilage or Starch.	Saccharine Matter or Sugar.	Gluten or Albumen.	Extract, or matter rendered insoluble during evaporation.
Middlesex Wheat, aver. crop	955	765	—	190	—
Spring Wheat	940	700	—	240	—
Mildewed Wheat of 1806	210	178	—	32	—
Blighted Wheat of 1804	650	520	—	130	—
Thick-skinned Sicilian Wheat of 1810	955	725	—	230	—
Thin-skinned Sicilian Wheat of 1810	961	722	—	239	—
Wheat from Poland	950	750	—	200	—
North American Wheat	955	730	—	225	—
Norfolk Barley	920	790	70	60	—
Oats from Scotland	743	641	15	87	—
Rye from Yorkshire	792	645	38	109	—
Common Bean	570	426	—	103	41
Dry Peas	574	501	22	35	16
Potatoes	{ from 260 to 200	{ from 200 to 155	{ from 20 to 15	{ from 40 to 30	—
Linseed Cake	151	123	11	17	—
Red Beet	148	14	121	14	—
White Beet	136	13	119	4	—
Parsnip	99	9	90	—	—
Carrots	98	3	95	—	—
Common Turnips	42	7	34	1	—
Swedish Turnips	64	9	51	2	2
Cabbage	73	41	24	8	—
Broad-leaved Clover	39	31	3	2	3
Long-rooted Clover	39	30	4	3	2
White Clover	32	29	1	3	5
Sainfoin	39	28	2	3	6
Lucerne	23	18	1	—	4
Meadow Fox-tail Grass	33	24	3	—	6
Perennial Rye Grass	39	26	4	—	5
Fertile Meadow Grass	78	65	6	—	7
Roughish Meadow Grass	39	29	5	—	6
Crested Dog's-tail Grass	35	28	3	—	4
Spiked Fescue Grass	19	15	2	—	2
Sweet-scented Soft Grass	82	72	4	—	6
Sweet-scented Vernal Grass	50	43	4	—	3
Fiorin	54	46	5	1	2
Fiorin cut in Winter	76	64	8	1	3

Among the substances associated in vegetable juices with gluten and albumen, is elastic gum or *Caoutchouc*, which has already been noticed as a binary compound of hydrogen and carbon. It is the produce chiefly of two trees growing in Brazil, the *hevea caoutchouc* and the *iatropha elastica*, the sap of which is milky and coagulable, and also abounds in albumen. Mr. Faraday has examined the sap of the Mexican caoutchouc-tree. (*Quarterly Journal*, xxi. 19.) It is pale yellow, creamy, and smells like sour milk. Its specific gravity 1011.74. Exposed to air, it deposits caoutchouc in successive films; and when heated, the caoutchouc also separates, and the substances associated with it remain in solution. 1000 parts of the original sap contained

Caoutchouc	317.0
Albumen	19.0
Bitter colouring matter, containing much nitrogen } wax	71.3
Matter soluble in water and not in alcohol . . .	29.0
Water, acid, &c.	563.7
	<hr/> 1000

Caoutchouc is very inflammable, burning with a red smoky flame. It fuses at a temperature nearly equal to that of melting lead, and forms a viscid liquid, sometimes used as a varnish to protect iron from rust. It is quite insoluble in water and in alcohol, but it dissolves sparingly in ether which has been washed with water, and the liquid, on evaporation, leaves a thin film of elastic and unaltered caoutchouc. Some of the volatile oils dissolve it, especially the oil of cajeput, but when evaporated they leave it in a viscid state, useless as a varnish. It dissolves in naphtha and in the oil of coal-tar. Caoutchouc is manufactured in a variety of forms by Mr. Hancock, and is applicable to many useful purposes in the chemical laboratory. (See FARADAY'S *Manipulation*.—*Index*.)

Sect. VIII. EXTRACT—ULMIN—POLYCHROITE—HEMATIN
 —BITTER PRINCIPLE—NICOTIN—ASPARAGIN—FUNGIN
 —INULIN—EMETIN.

By the term *extract*, or *extractive principle*, we mean a substance contained in the greater number of vegetables, and generally forming the principal ingredient in the pharmaceuti- cal preparations called *extracts*. It possesses the following properties. It is soluble in water, and the solution is of a brown colour. It is insoluble in ether, but it is soluble in alcohol containing a small portion of water. By repeated solutions and evaporations it may be rendered scarcely soluble in water. Solutions of chlorine, of many of the acids, and of most of the metallic oxides, occasion precipitates in the aqueous solution of extractive. It combines with alumina, and is there- fore applicable as a brown dye-stuff. These characters are not, however, considered sufficiently definite to mark it as a distinct principle; on the contrary, they point out an analogy between extractive and tannin.

The following substances may be considered under this head, though many of them are obviously widely different from extractive matter.

Ulmin.—This substance was first noticed by Klaproth, spontaneously exuding from the elm. From the observations of Berzelius, it exists in the bark of many other trees, and may be obtained by digestion in alcohol and cold water; the action of hot water afterwards dissolves the ulmin.—THOM- SON'S *Annals*, vol. ii.

Ulmin is of a dark brown colour, with scarcely any taste or smell. It is sparingly soluble in water and in alcohol, but readily soluble in a weak solution of carbonate of potassa. Very few of the metallic salts occasion a precipitate in its solution. The exudation from the elm is generally combined with carbonate of potassa, and is therefore readily soluble in water. Nitric acid and solution of chlorine added to a solu- tion of ulmin occasion precipitates, the properties of which

approach those of a resin. (SMITHSON, *Phil. Trans.*, 1813.) Dobereiner converted gallic acid into ulmin. "The latter," he says, "consists of two proportionals of carbon, two of oxygen, and one of hydrogen." (*Ann. de Chim. et Phys.*, xxiv., 335.)

Polychroite.—This term has been applied to the extract of saffron. (*Annales de Chim.*, tom. lxxx.) It is of a deep yellow colour, deliquescent, readily soluble in water and in alcohol, but insoluble in pure sulphuric ether. Exposure to the solar rays soon destroys the colour of its aqueous solution. Sulphuric acid renders it blue, and nitric acid green: solutions of lime and baryta produce yellow and red precipitates: subacetate of lead throws down a deep yellow precipitate, and nitrate of mercury separates a red powder.

Hematin.—This peculiar substance was first recognised by Chevreul in the colouring matter of *logwood*. (*Ann. de Chim.* tom. lxxxi.) It may be obtained by digesting logwood in water of the temperature of 125°. Filter, evaporate carefully to dryness, and digest the residue for 24 hours in alcohol of the specific gravity of .837. Filter the alcohol; concentrate the solution by evaporation, add a portion of water, evaporate a little further, and set the solution aside: crystals are deposited which, when washed with alcohol and dried, are pure hematin.

Hematin is of a reddish colour; its taste is somewhat bitter, and its aqueous solution is yellow when cold, but orange-red at the temperature of boiling-water. Sulphuric acid added to this solution renders it reddish yellow. The alkalis give it a purplish tint.

Bitter principle.—By evaporating an infusion of quassia, a substance is obtained of an intensely-bitter taste, and of a brownish yellow colour, which is readily soluble in water and in alcohol. Nitrate of silver and acetate of lead are the only precipitants of its aqueous solution. It is probable that the same substance exists in other bitter vegetables, and Vauquelin has discovered it in the fruit of the *colocynth*, and in the root of *white briony*.—THOMSON'S *System*, vol. iv.

By digesting indigo, silk, and a few other substances in nitric acid, an intensely-bitter matter is formed, called by Welther the *yellow bitter principle*. (*Annales de Chim.* tom. xxix.) Chevreul has rendered it probable that this is a com-

pound of a peculiar vegetable principle with nitric acid. It is crystallizable, burns like gunpowder, and detonates when struck with a hammer.

Picrotoxine.—This is a bitter poisonous substance contained in the *Cocculus Indicus*. It may be obtained by the following process:—Add acetate of lead to a decoction of the berries, as long as any precipitate falls: filter, evaporate, and digest the extract in highly-rectified alcohol; evaporate to dryness, and agitate the remaining matter with a little water; the picrotoxine remains in the form of white prismatic crystals of a bitter taste.

Picrotoxine is difficultly soluble in water. Alcohol, of the specific gravity of 810, dissolves one-third its weight. It is soluble in weak solutions of the pure alkalis. Picrotoxine has sometimes been described as a salifiable base, and been supposed united in the seeds to a peculiar acid, which has been termed *menispermic acid*. Casaseca has shown that this acid does not exist, and that picrotoxine does not form definite compounds with the acids. (*Ann. de Chim. et Phys.* xxx.)

Nicotin.—This is a principle existing in tobacco. It was obtained by Vauquelin by the following process (*Ann. de Chim.* lxxi.): Evaporate the expressed juice of fresh tobacco leaves to one-fourth its bulk; and, when cold, strain it through fine linen; evaporate nearly to dryness; digest the residue in alcohol; filter and evaporate to dryness; dissolve this again in alcohol, and again reduce it to a dry state. Dissolve the residue in water, and saturate the acid which it contains with weak solution of potassa, introduce the whole into a retort, and distil to dryness; redissolve, and again distil three or four times successively. The nicotin will thus pass into the receiver, dissolved in water, from which solution it may be obtained by very gradual evaporation.

Nicotin is colourless, acrid, soluble in water and in alcohol, volatile, and highly poisonous.

Pollenin.—Dr. John discovered a peculiar matter in the pollen of the tulip, to which he gave the above name. It is insoluble in water, alcohol, ether, oils, and alkalis; and, when distilled, yields ammonia and an acid liquor. Thrown into the flame of a candle it burns rapidly with a kind of deflagration; hence, the pollen of *licopodium* is occasionally used to produce

theatrical lightning: it is much cleaner, and more brilliant and rapid in its combustion, than resin.

Asparagin.—MM. Vauquelin and Robiquet obtained this substance in a crystalline form by evaporating the juice of asparagus. It has a cool and slightly nauseous taste, and when burned emits acrid vapours, and leaves no traces of alkali.—(*Annales de Chimie*, tom. iv.) Asparagin has also been found in liquorice and in marshmallow.

According to Plisson, when asparagin is digested in a mixture of hydrated protoxide of lead and water, a compound is formed, which may be decomposed by the action of sulphuretted hydrogen. A peculiar acid is thus obtained in prismatic crystals, difficultly soluble in cold water, and insoluble in alcohol. This he calls the *aspartic acid*, and has described its combination with bases under the name of *aspartates*. (*Ann. de Chim. et Phys.*, xl. 309.)

Fungin.—This name has been given by Braconnot to a substance contained in the fleshy part of mushrooms. (*Ann. de Chim.* lxxix.) It is insoluble in water and in alcohol, and scarcely acted upon by the alkalis, or by dilute acids. It is the substance which remains after the mushroom has been deprived of every thing soluble in alcohol and in water.

Legumine.—Braconnot has given this term to a substance which he separated from pease. It appears to exist, generally, in the leguminous vegetables. (*Ann. de Chim. et Phys.*, xxxiv. 68.)

Inulin.—The roots of elecampane, when boiled in water, furnish a decoction, which, on cooling, deposits a white powder, in many respects resembling starch. It, however, differs in several properties from that principle, and has hence been considered a peculiar vegetable substance.—THOMSON'S *System*, vol. iv.

Dahline, extracted by Payen from Dahlia roots, is a principle much resembling inulin. (*Ann. de Chim. et Phys.*, xxiv. 209.)

Emetin.—To obtain emetin, digest powdered ipecacuanha in alcohol, filter, evaporate carefully to dryness, and redissolve in cold water. To this solution add carbonate of baryta, filter, and again evaporate to dryness; digest this residuum in alcohol, and a solution is obtained, which, by careful evaporation,

affords a reddish-brown substance, soluble in alcohol and in water, and precipitable by sub-acetate of lead; its taste is acrid and bitter, and it is highly emetic.—MM. MAGENDIE and PELLETIER, *Annales de Chimie et Physique*, vol. iv.

Section IX. LIGNIN—CORK—COTTON—MEDULLIN.

THE term *lignin* has been applied to the insipid and insoluble fibrous substance which remains after repeatedly digesting wood in water and in alcohol till all matters soluble in those fluids have been removed. It is insipid, and, exposed to destructive distillation, affords a considerable quantity of vinegar tainted by empyreumatic oil, and containing a little ammonia. This liquor was formerly known under the name of *pyroligneous acid*. (See *Acetic Acid*.) The charcoal which remains is light, brittle, shining, and easily incinerated. The relative quantity of carbon, yielded by different woods, has already been adverted to. (See *Carbon*.)

Among the results of the destructive distillation of wood, Mr. P. Taylor first noticed a curious product, which has since been termed *pyroxylic spirit*. It is colourless and transparent, and, when rectified, has an average specific gravity of .820. Its taste and smell are strong and pungent. It boils at about 150°, and burns with a blue flame, leaving no residue. Its properties have been studied by MM. Macaire and Marcet. (*Ann. of Phil.*, N. S., viii. 69.) It dissolves in alcohol, but not in oil of turpentine, and when distilled with sulphuric acid does not afford ether or olefiant gas. Distilled with nitric acid, and with chlorine, it affords peculiar ethereal fluids. Its ultimate elements appear to be

6	proportionals of carbon	.	(6 × 6) =	36
4	„ oxygen	.	(8 × 4) =	32
7	„ hydrogen	.	.	= 7
				<hr/> 75

We are indebted to M. Braconnot for some highly-interesting experiments, relating to the action of sulphuric acid on

wood. (*Ann. de Chim. et Phys.*, xii. 172.) In the course of these researches, he triturated 25 parts of hempen cloth with 34 of the acid : it acquired the consistency of mucilage, which, after 24 hours, was almost entirely soluble in water. The diluted liquor was saturated with chalk, filtered, and evaporated to the consistency of syrup ; it deposited sulphate of lime, and was then further evaporated to dryness, when a substance, having the characters of gum, was obtained. In another experiment, 24 parts of lignin were reduced to gum by 34 of sulphuric acid ; this acid mixture, diluted with water, and boiled for 10 hours, became sweet ; the acid was then separated by chalk, and the liquor, on due evaporation, afforded a crystallizable sugar.

Moistened saw-dust, heated in a platinum crucible with its weight of caustic potassa, afforded a matter soluble in water, and which, upon the addition of an acid to neutralize the alkali, yielded a substance having the properties of *ulmin*.

When nitric acid is digested upon lignin, it forms oxalic, malic, and acetic acids. Long exposed to air and moisture, lignin crumbles down into a black pulverulent mould ; but if air be excluded, it suffers little change, even though moisture be present.

Some years ago Professor Autenrieth, of Tubingen, showed, that by proper management lignin might be converted into a species of palatable and nutritious bread. The following was his process :—

“ In the first place, every thing that was soluble in water was removed by frequent maceration and boiling. The wood was then reduced to a minute state of division, that is to say, not merely into fine fibres, but actual powder ; and after being repeatedly subjected to the heat of an oven, was ground in the usual manner of corn. Wood thus prepared, according to the author, acquires the smell and taste of corn flour. It is, however, never quite white, but always of a yellowish colour. It also agrees with corn flour in this respect, that it does not ferment without the addition of leaven, and in this case sour leaven of corn flour is found to answer best. With this it makes a perfectly uniform and spongy bread ; and when it is thoroughly baked, and has much crust, it has a much better taste of bread than what in times of scarcity is prepared from

the bran and husks of corn. Wood flour also, boiled in water, forms a thick, tough, trembling jelly, like that of wheat starch, and which is very nutritious." (PROUT, *Phil. Trans.* 1827.)

With regard to the ultimate elements of lignin, Gay-Lussac and Thenard first showed that the hydrogen and oxygen in this principle exist in it in the proportions in which they form water—a result confirmed by subsequent experiments. The variety of forms in which lignin occurs in different woods is so great, as to put an examination of them all out of the question; Dr. Prout therefore selected two for the purpose of analysis, *viz.* the woods of the *Box* and *Willow*, which appeared to present the greatest contrast; the one being among the densest, the other the lightest of the woods. These were both treated exactly in the same manner, that is to say, they were first reduced to the form of a coarse powder by rasping, then well pulverized in a Wedgwood mortar, and afterwards sifted. Being by these means reduced to the form of impalpable powders, they were boiled in repeated portions of distilled water, till that fluid came off unchanged. After this they were similarly treated with alcohol, and finally again with distilled water. They were now exposed to the atmosphere, when in a dry and favourable state; and when they ceased to lose weight were submitted to analysis, and found to consist of (abstracting foreign matters)

	Box.	Willow.
Carbon . . .	42.7	42.6
Water . . .	57.3	57.4

A known weight of each was then exposed for twenty-four hours to a temperature of 212° , and afterwards for six hours longer (by means of an oil bath) to a temperature between 300° and 350° ; and at the end of this time they were found to have lost, *per cent.*,

Box.	Willow.
14.6	14.4

Analysed in this state of desiccation, they were found to consist of

	Box.	Willow.
Carbon . . .	50.0	49.8
Water . . .	50.0	50.2

showing that the loss of weight arose from the escape of water. These latter results nearly agree with those of MM. Gay-Lussac and Thenard, as obtained from the analyses of the

woods of the *Oak* and *Beech*, and seem to show, beyond a doubt, that the composition of all of them is similar, or that they consist of equal weights of carbon and water; to which simple analogy, Dr. Prout observes, this important principle probably owes its stability.

Suber or *Cork*.—This is a light, soft, elastic, and combustible substance, burning with a bright flame and leaving a bulky charcoal. Its principal peculiarity is, that by digestion in nitric acid it is converted into an orange-coloured mass, which furnishes to water a peculiar acid matter, which has been termed *suberic acid*. Chevreul has found in it resin, oil, and a peculiar matter which he calls *Cerin*.—See WAX.

Cotton is a downy substance found in the seed-pods of the different species of *gossypium*. It is insoluble in water and in dilute alkaline and acid solutions. It combines with several of the metallic oxides, which are therefore used as intermedes, or *mordants*, in the art of dyeing. Acetate of alumina is principally employed for this purpose.

Medullin is a term given by Dr. John to the pith of the sun-flower, and some other plants; it is insipid, inodorous, insoluble in water and alcohol, and affords oxalic acid when treated by nitric acid; submitted to destructive distillation, the products abound in ammonia.

Section X. TANNIN.

TANNIN, or the astringent principle, is contained in many vegetables. It may be procured by digesting bruised gall-nuts, grape-seeds, oak-bark, or catechu, in a small quantity of cold water. The solution affords, when evaporated, a substance of a brownish-yellow colour, extremely astringent, and soluble in water and in alcohol.

The purest form of tannin appears to be that derived from bruised grape-seeds, but even here it is combined with other substances, from which it is perhaps scarcely separable; and among the numerous processes which have been devised for procuring pure tannin, there is none which appears to me completely to answer the intended purpose. I have never

been able to obtain it of greater apparent purity than by digesting powdered catechu in water at 33° or 34°, filtering and boiling the solution, which, on cooling, becomes slightly turbid, and is to be filtered again, and evaporated to dryness. Cold water, applied as before, extracts nearly pure tannin.

Berzelius, in his *Lehrbuch*, has given several processes for the preparation of tannin, two of which are as follows:—

“ *First method.* A hot infusion of gall-nuts is to be filtered through a cloth, a very small quantity of weak sulphuric acid added, and the whole well mixed; the coagulum formed is to be separated, and the liquid filtered. Sulphuric acid, diluted with half its weight of water, is to be added in small quantities with agitation; the precipitate, after an hour's rest, acquires a half-fluid glutinous state; then the fluid is to be decanted, and carefully mixed with concentrated sulphuric acid, as long as any precipitate is formed. It is a compound of sulphuric acid and tannin, yellowish-white, and insoluble in a weak acid. Being put on a filter, it is to be washed with diluted sulphuric acid, pressed between bibulous paper, dissolved in pure water, and carbonate of lead in fine powder added to the fluid, until the free sulphuric acid is neutralized; ebullition for a short time also removes the acid combined with the tannin; perfect saturation is indicated by the deep yellow colour taken by the solution. The filtered fluid is to be evaporated carefully to dryness in an air-pump if possible; the brown extract obtained pulverized, and digested in ether, at a temperature of 86° Fahr. The ethereal solution evaporated yields a pale yellow transparent substance, which is pure tannin. It suffers no change in the air.

“ *Second method.* A concentrated solution of carbonate of potash is to be added to a filtered infusion of galls, only as long as a white precipitate is formed. The precipitate is to be washed on a filter with ice-cold water, and then dissolved in weak acetic acid. By filtration a brown matter is separated; the clear fluid is to be precipitated by acetate of lead; the compound of tannin and oxide of lead washed, and then decomposed by sulphuretted hydrogen. The filtered liquid is then colourless, and, being evaporated under the air-pump receiver, gives transparent yellowish hard scales, which, treated with ether as before, yield pure tannin.

“ Pure tannin is colourless, but sometimes becomes coloured by alteration in the air ; it is not deliquescent, is easily pulverized, and dissolves readily in water. By distillation it yields no ammonia, but a yellow oil and a liquid, which, on cooling, deposit crystals different from those of gallic acid : they have a hot taste, and colour or precipitate salts of iron of a yellowish or greyish green.

“ The combinations of tannin with acids, when exactly saturated, have no sourness, but a pure astringent taste. When pure, they are usually very soluble in water, and precipitated only by a great excess of acid. With salifiable bases, tannin forms very curious compounds. The neutral compound with potash or ammonia is little soluble in cold water, more so in hot, separating from the latter, as the temperature diminishes, in the form of a white powder, which, put in the filter, pressed, and dried, looks like an earthy salt, and remains unchanged in the air. When moist, it forms extract by means of the air. The combination with soda is much more soluble.”

The most distinctive character of tannin is that of affording an insoluble precipitate when added to a solution of isinglass, or any other animal jelly. Upon this property the art of tanning depends, for which oak-bark is generally employed ; the barks, however, of many other trees may occasionally be substituted. The following Table, drawn up by Sir Humphry Davy, exhibits the average quantity of tan contained in 480lbs. of different barks.—*Agricultural Chemistry*, 4to., p. 79.

	lbs.
Average of entire bark of middle-sized Oak, cut in spring	29
„ Spanish Chestnut	21
„ Leicester Willow, large size	33
„ Elm	13
„ Common Willow, large	11
„ Ash	16
„ Beech	10
„ Horse Chestnut	9
„ Sycamore	11
„ Lombardy Poplar	15
„ Birch	8
„ Hazel	14
„ Black Thorn	16
„ Coppice Oak	32
„ Oak, cut in autumn	21
„ Larch, cut in autumn	8
White interior cortical layers of Oak-bark	72

Tan forms a precipitate with solution of starch, with gluten and albumen, and with many of the metallic oxides. An account of the precipitates formed in metallic solutions by infusion of galls, will be found under the article *Gallic Acid*; but these precipitates are very complex, and vary in composition. Its compounds with the salifiable bases generally have been termed *Tannates*.

If the solution of tan, obtained as above described from catechu, be added to acetate of lead, an insoluble *tannate of lead* falls, composed, according to Berzelius, of 100 tannin + 52 oxide of lead. Now, if we suppose that tannin forms definite compounds with the metallic oxides, in the manner of a vegetable acid, the number 215 will be its representative, as deduced from the above datum; for $52 : 100 :: 112 : 215$.

The ultimate constituents of tan are stated by Berzelius to be,

Carbon	50.55
Oxygen	45.00
Hydrogen	4.45
						<hr/>
						100

Artificial Tan.—Mr. Hatchett has shown that tan may be formed artificially by digesting charcoal in dilute nitric acid during several days; it is at length dissolved, and a reddish-brown liquor is obtained, which furnishes, by careful evaporation, a brown glossy substance, amounting to about 120 parts from 100 of charcoal.

This *artificial tannin* appears to differ in one circumstance only from natural tannin, which is, that it resists the action of nitric acid, by which all the varieties of natural tannin are decomposed, though some are more capable of resisting its action than others.

Artificial tannin has a bitterish astringent taste, is soluble in water and alcohol, and forms an insoluble precipitate in solutions of animal gelatine, the precipitate consisting, according to Mr. Hatchett, of

36 tannin
64 gelatine
<hr/>
100

Muriatic and sulphuric acids occasion brown precipitates, in solution of artificial tan, which are soluble in hot water.

It combines with the alkalis, and forms a precipitate of difficult solubility in aqueous solutions of lime, baryta, and strontia, and in most metallic solutions: these precipitates are of a brown colour.

A variety of artificial tan is formed by digesting camphor and resins in sulphuric acid, till the liquor becomes black, and on being poured into water, deposits a black powder, which, by digestion in alcohol, furnishes a brown matter, soluble in water, and forming an insoluble precipitate with gelatine.—HATCHETT, *Phil. Trans.* 1805, 1806,

Section XI. COLOURING MATTER.

THE colouring matter of vegetables appears to reside in several of their principles, and is therefore very differently acted on by solvents. Its extraction, and transfer to different substances, constitutes the *art of Dyeing*.

The principles of this art can here only be generally stated; for practical details the reader is referred to an Essay in the *Manchester Memoirs* (vol. iii.); to Dr. Bancroft's work on *Permanent Colours*; to the treatise of Berthollet, which has been translated by Dr. Ure; and to a paper, by Thenard and Roard, in the 74th volume of the *Annales de Chimie*.

The goods to be dyed require to be thoroughly cleansed from all foreign matters and colours, which is effected by washing and *bleaching*. Warm water is at first liberally applied to remove the filth acquired in weaving; the goods, if linen or cotton, are then *bowked*, or boiled with a very weak solution of caustic potassa, washed in large quantities of water, and spread out upon the grass so as to be exposed freely to the joint agencies of light, air, and moisture; this part of the operation, which is tedious, may be much curtailed, or even superseded, by the careful application of a weak solution of chloride of lime. The bowking and exposure are alternately repeated as often as necessary; and lastly, the goods are immersed in water slightly acidulated by sulphuric acid, again thoroughly washed, and dried. By these operations, the tex-

ture of the stuffs is always more or less impaired, especially when chloride of lime is used.

In respect to the theory of the operation of bleaching, it appears, I think, that in the necessary exposure to water, air, and light, or the substitute of chlorine, nascent oxygen is developed, and is the destroyer of those portions of colouring matter which are most obstinately retained.

Different materials not only possess very different attractions for dye stuffs, but they absorb the colouring matter in very different proportions. Wool appears in this respect to have the strongest attraction for colouring substances; silk comes next to it; then cotton; and lastly, hemp and flax.

Colours have been divided by Dr. Bancroft, in his work on *Permanent Colours*, into *substantive* and *adjective*. The former communicate colour without the intervention of any other substance. They have an attraction for the fibre of cloth or linen, and are permanently retained. The latter require the intervention of some body, possessed of a joint attraction for the colouring material and stuff to be dyed. The substance capable of thus fixing the colour, has been called a *basis*, or *mordant*.

The mordants most frequently employed are *acetate of alumina*, *sulphate* or *acetate of iron*, and *muriate of tin*. The substance to be dyed is first impregnated with the mordant, and then passed through a solution of the colouring matter, which is thus fixed in the fibre, and its tint is either modified or exalted by the operation.

That a considerable portion of the mordant is retained in the fibre of the calico or cloth dyed, has been proved by the experiments of Dr. Ure. He found that 100 parts of the ashes of Turkey-red calico (dyed by an alum mordant) afforded between 16 and 17 parts of alumina; whereas the ashes of white and washed calico only afforded a trace of that earth. (See two papers, by Dr. Ure, on the incinerated ashes of cotton-wool and calico dyed by the Turkey-red process. (*Quart. Journ.*, xxi. 28—297.)

The following are the modes of producing some of the principal colours:—

† *Black* is produced by astringents and salts of iron; and if intended to be deep and perfect, the cloth should previously

be dyed blue with indigo. The stuff is first soaked in a bath of galls, then rinsed, and passed repeatedly through a solution of sulphate of iron in infusion of logwood; exposure to air deepens the colour, which at first has a purplish tint. Logwood tends considerably to improve the black, and prevents its acquiring a rusty or brown hue. Sometimes madder is used for the same purpose. Silk is dyed black nearly in the same way, but it requires a much larger relative proportion of galls, and the operation must be frequently repeated. It is difficult to give a good and permanent black to calico; in this process, acetate of iron, galls, and madder are generally used, and the colour is rendered more durable by previously steeping the goods in a weak solution of glue.

Grey is produced by the same operations as black, but the materials are used in a very dilute state.

Blue is chiefly derived from *indigo*, a substance produced by fermenting the leaves of several species of the *indigofera*, a plant abundantly cultivated in South America and in the East Indies.

Indigo is a substance of a deep blue colour, containing about 50 *per cent.* of pure colouring matter, which is perfectly insoluble in water; when heated to between 500° and 600°, it affords a sublimate in the form of a blue smoke, which, on condensation, forms acicular crystals, amounting in weight to 18 or 20 *per cent.* of the original indigo. It is soluble in concentrated sulphuric acid. This solution is usually called *Saxon* or *liquid blue*, and is used as a substantive colour for dyeing cloth and silk. Substances which powerfully attract oxygen render indigo green, and by exposure to air, it again acquires a blue colour. In this green state indigo is soluble in the alkalis, and the solution is commonly employed for dyeing calico. A bath for this purpose may be made by mixing one part of indigo, two parts of sulphate of iron, and two of lime, in a sufficient quantity of water: in this case, the sulphate of iron is decomposed by a portion of the lime. The protoxide of iron thus produced becomes peroxidized at the expense of the indigo, which is rendered green and soluble in the alkaline liquor; cotton steeped in this solution acquires a green colour, which, by exposure to air, and washing in water acidulated with sulphuric acid, becomes a permanent blue.

A little iron or zinc thrown into diluted sulphate of indigo changes or destroys the colour in consequence of the evolution of hydrogen; the colour is also quickly impaired and destroyed by chlorine.

The analysis of indigo, to ascertain the proportion of colouring matter, which varies much in different samples, may be performed by the successive action of water, alcohol, and muriatic acid. (Chevreul, *Ann. de Chim.* lxxi. 20.) 100 parts of Guatemala indigo, thus treated, afforded

To Water..	{ Green matter combined with ammonia. Deoxidized indigo Extract Gum }	12
To Alcohol.	{ Green matter Resin A trace of indigo }	30
To Muriatic Acid	{ Red resin Carbonate of lime Oxide of iron Alumina }	6 2 2
Residue . . .	{ Silica Pure Indigo }	3 45
		100

A great variety of experiments have been made by different chemists upon indigo, of which it is not easy to make an intelligible extract: perhaps the following are the most essential results. In regard to the manufacture of indigo, two papers will be found in the *Quarterly Journal* (vols. v. 296, and vi. 265, *N. S.*), detailing the principal steps of the operation and the probable nature of the results.

The action of Sulphuric Acid upon Indigo, a subject of much importance to the dyer, has been investigated by Mr. Crum (*Ann. of Phil.*, N. S., v. 81). The concentrated acid does not merely dissolve it, but, in the course of twenty-four hours, alters its properties; it at first becomes yellow, in consequence probably of the abstraction of the elements of water, for much heat is evolved, and the addition of water instantly restores the blue tint. Nothing is evolved or absorbed, nor is carbon precipitated. When the sulphuric solution is neutralized by potassa, an intensely blue precipitate

falls, soluble in water, but insoluble in saturated solutions of the salts of potassa; it was therefore purified by alternate washing with solution of acetate of potassa and alcohol. When dry it acquires a copper colour, is very hygrometric, soluble in 140° of cold and in a smaller proportion of hot water. The cold solution, even when largely diluted, furnishes insoluble precipitates with salts of potassa, soda, lime, baryta, strontia, lead, and mercury. This substance has been called *Cerulin*, and exists in the precipitate as a *ceruleo-sulphate of potassa*: it appears to be a hydrate of indigo, in which one proportional of indigo is combined with four of water.

By limiting the action of the acid upon the indigo to three or four hours (or at 100° to 20 minutes), different results are obtained. One part of purified indigo was shaken in a phial with ten of sulphuric acid till it became green, it was then poured into water, and filtered. The first washings of the substance upon the filter are to be rejected; but when the liquid passes of a blue colour, solution of chloride of potassium may be added, which throws down a *purple* precipitate, called by Mr. Crum, *Phenicin* (from φαινξ).

This substance is soluble in water and alcohol; it is converted by sulphuric acid into cerulin; it is precipitated by almost all saline substances of a purple colour; it appears to contain one proportional of indigo and two of water.

According to Crum, the *blue sublimate of indigo* consists of

Carbon	73.22
Oxygen	12.60
Nitrogen	11.26
Hydrogen	2.92
						<hr/>
						100

These numbers may be considered as nearly equivalent to

16	proportionals of carbon	.	.	=	96
2	" oxygen	.	.	=	16
1	" nitrogen	.	.	=	14
4	" hydrogen	.	.	=	4
					<hr/>
					130

So that, upon this view of the subject, the equivalent representative of pure indigo would be 130.

Indigo has also been subject to an interesting series of experiments by Berzelius (*Ann. de Chim. et Phys.*, Nov. et Dec. 1827), who found its usual constituents to be four distinct substances: viz. gluten; a peculiar brown substance, apparently resembling extract; a red substance, which gives a white sublimate when heated in close vessels; and pure indigo.

The deoxidizement and consequent solubility of indigo have already been referred to: this, and the action of nitric acid upon indigo, has been satisfactorily inquired into by M. Liebig (*Ann. de Ch. et Phys.* xxxv.) Deoxidized indigo he obtained as follows:—

1½ part of pure indigo, 2 parts of proto-sulphate of iron, 2½ parts of hydrate of lime, and from 50 to 60 parts of water, were digested together for 24 hours in a close vessel, which had previously been filled with hydrogen. The clear liquor over the sulphate of lime and oxide of iron had a yellowish-red colour, and was separated by a syphon filled with hydrogen, and mixed with diluted muriatic acid, containing some sulphite of ammonia dissolved; a dense white precipitate was formed, becoming blue in the air. This was gathered in a filter out of contact of air, and washed with boiled water containing sulphite of ammonia in solution, and dried at 212°, in close vessels through which a current of hydrogen was continually passed. The upper surface of the mass became of a blue colour, but the lower remained of a dull white.

This white substance was called *Indigogene*. It did not change colour in dry air, but under water became of a deep blue, which by drying assumed a coppery appearance. The blue substance volatilized by heat without leaving any residue, forming purple vapours, which condensed, when cold, into crystals differing in nothing from sublimed indigo. Indigogene dissolves in alkalis without neutralizing them: it is also soluble in alcohol, but insoluble in water or acids.

A given quantity of this indigogene was acted upon by ammonia, and the weight of the undissolved blue portion ascertained; it appeared that the weight of the pure portion dissolved was 0.404 grammes (6.224 grains). The solution was put into an inverted jar, over mercury, and oxygen gas gradually passed in until absorption ceased, and then the liquid containing the precipitated indigo was evaporated to dryness at 212°. The

weight of the substance was increased to 0.047, *i. e.* 11.5 per cent.

Not having obtained indigogene *perfectly* pure, M. Liebeg did not attempt to analyze it for the ultimate composition. He remarks, that indigo is, perhaps the only organic body from which one of its constituent parts may be taken without total decomposition; and which, by oxidation, passes to the state of a body, having much analogy with peroxides.

The action of nitric acid on indigo has been particularly examined by Mr. Hatchett (*Additional Experiments on Artificial Tannin*, *Phil. Trans.* 1805). This acid, diluted with about two parts of water, produces much effervescence when poured on powdered indigo, and gradually dissolves it; the solution, evaporated to dryness, leaves a yellow residue, soluble in water, of an intensely bitter taste, and composed partly of artificial tannin, and partly of a peculiar *bitter principle* combined with ammonia.

The action of nitric acid on indigo has also been studied by Liebeg, who finds a peculiar acid among the results afforded by treating indigo with excess of nitric acid, which he terms *Carbazotic acid*, and respecting the production and properties of which he has given the following details:—

A portion of the best indigo is to be broken into small fragments, and moderately heated with eight or ten times its weight of nitric acid of moderate strength. It will dissolve, evolving an abundance of nitrous vapours and swelling up in the vessel. After the scum has fallen, the liquid is to be boiled, and nitric acid added, whilst any disengagement of red vapours is occasioned by it. When the liquid has become cold, a large quantity of semi-transparent yellow crystals will be formed, and if the operation has been well conducted, no artificial tannin or resin will be obtained. The crystals are to be washed with cold water, and then boiled in water sufficient to dissolve them. If any oily drops of tannin form on the surface of the solution, they must be carefully removed by touching them with filtering paper. Then filtering the fluid, and allowing it to cool, yellow brilliant crystalline plates will be obtained, which will not lose their lustre by washing.

To obtain the substance perfectly pure, the crystals must be re-dissolved in boiling water, and neutralized by carbonate

of potash. Upon cooling, a salt of potash will crystallize, which should be purified by repeated crystallizations.

On mixing the first mother liquor with water, a considerable brown precipitate will be obtained, which being dissolved in boiling water, and neutralized by carbonate of potash, will furnish a large quantity of the potash salt. All the potash salt obtained in these operations is to be re-dissolved in boiling water, and nitric, muriatic, or sulphuric acid added; as the solution cools, the peculiar substance will be observed to form very brilliant plates of a clear yellow colour, generally in equilateral triangular forms.

Sometimes crystals are not formed after the action of the nitric acid on the indigo, in which case, the liquor must be evaporated, and water added, when the substance will precipitate, and must be purified as already described. Four parts of indigo yield one of the pure substance.

When the substance is heated, it fuses, and is volatilized without decomposition; when subjected to a sudden strong heat, it inflames without explosion, its vapours burning with a yellow flame, and a carbonaceous residue remaining. It is but little soluble in cold water, but much more in boiling water; the solution has a bright yellow colour, reddens litmus, has an extremely bitter taste, and acts like a strong acid on metallic oxides, dissolving them, and forming peculiar crystallizable salts. Ether and alcohol dissolve the substance readily. When fused in chlorine or with iodine, it is not decomposed, nor does solution of chlorine affect it. Cold sulphuric acid has no action on it; when hot, it dissolves it, but water separates the substance without alteration. Boiling muriatic acid does not affect it, and nitro-muriatic acid only with great difficulty.

These results show that no nitric acid is present in the substance, and other experiments prove that no oxide of nitrogen exists in it; it contains no oxalic or other organic acid, for when its salt is boiled with chloride of gold, the latter is not reduced.

When heated to redness with oxide of copper, it gave a mixture of nitrogen and carbonic acid, in the exact proportion of one volume of the former to five of the latter. This was a

constant result, and in no case was any sulphuric or muriatic acid left in the copper. 0.0625 grammes of the substance thus decomposed gave 45 cubic centimeters of the mixed gases, estimated at 0° C. (32° F.) and the pressure of 28 inches of mercury; according to which, the acid would be composed of carbon 32.392, nitrogen 15.2144, oxygen 52.3936 *per cent.* Its composition is as follows by experiment and theory:—

				Theory.					
Carbon	.	.	35.043	.	36.081	.	15 atoms	.	114.65
Azote	.	.	16.167	.	16.714	.	3	„	53.11
Oxygen	.	.	48.790	.	47.205	.	15	„	150.00
<hr/>				<hr/>				<hr/>	
100.000				100.000				317.76	

100 parts of the acid neutralize a quantity of base equivalent to 3.26 of oxygen, which is to the oxygen of the acid as 1 : 16; the equivalent number of the acid derived from the analysis of the barytic salt was 306.3; by adding only $\frac{1}{4}$ *per cent.* to the quantity of baryta obtained in the experiment, 317.76, or the number expressed by the above formula, would be obtained.

When a salt of potash or baryta was decomposed by oxide of copper and heat, the quantity of carbonic acid produced was a little short of five times the quantity of nitrogen; but upon adding that retained by the alkali or earth, the proportion became exactly the same as in the former cases.

Welter's bitter principle was prepared by acting on silk with ten or twelve times its weight of nitric acid. The liquid, slightly coloured at first, acquired a deep yellow upon adding water. It was neutralized by carbonate of potash whilst hot, and left to cool, and the salt of potash thus obtained, decomposed by muriatic, nitric, or sulphuric acid. This acid, crystallized like that from indigo, formed the same salts, and was composed in the same manner. Silk, however, furnishes much less of the substance than indigo. The most important salts formed by the carbazotic acid have the following properties:—

“ *Carbazotate of Potash* crystallizes in long yellow quadrilateral needles, semi-transparent and very brilliant; it dissolves in 260 parts of water at 60° F., and in much less boiling

water: a saturated boiling solution becomes a yellow mass of needles, from which scarcely any fluid will run. Strong acids decompose it; yet when an alcoholic solution of carbazotic acid is added to a solution of nitre, crystallized carbazotate of potash, after some time, precipitates. Alcohol does not dissolve it. When a little is gradually heated in a glass tube, it first fuses, and then suddenly explodes, breaking the tube to atoms; traces of charcoal are observed on the fragments. This salt precipitates a solution of the protonitrate of mercury, but not salts, containing the peroxide, or those of copper, lead, cobalt, iron, lime, baryta, strontia, or magnesia. The slight solubility of this salt supplies an easy method of testing and separating potash in a fluid. Even the potash in tincture of litmus may be discovered by it; for, on adding a few drops of carbazotic acid, dissolved in alcohol, to infusion of litmus, crystals of the salt gradually separated. The saturated solution of the salt at 50° F. is not troubled by muriate of platina. The salt contains no water of crystallization. It was analyzed by converting a portion of it into chloride of potassium by muriatic acid. Its composition is,—

Carbazotic acid	83.79
Potash	16.21
					<hr/> 100.00

Carbazotate of Soda crystallizes in fine silky yellow needles, having the general properties of the salt of potash, but soluble in from 20 to 24 parts of water, at 59° F.

“ *Carbazotate of Ammonia* forms very long, flattened, brilliant, yellow crystals, very soluble in water. Heated carefully in a glass tube, it fuses, and is volatilized without decomposition; heated suddenly, it inflames without explosion, and leaves much carbonaceous residue.

Carbazotate of Baryta is obtained by heating carbonate of baryta and carbazotic acid with water. It crystallizes in quadrangular prisms of a deep colour, and dissolves easily in water. When heated, it fuses, and is decomposed with very powerful explosion, producing a vivid yellow flame: the explosion is as powerful as that of fulminating silver. A solution of chloride of potassium, to which carbazotate of baryta has

been added, produces a precipitate of the potash salt, and not more than $1\frac{1}{2}$ per cent. of potash remains in solution. 100 parts of the crystallized salt contain,—

Carbazotic acid	.	69.16	oxygen of the acid	.	16
Baryta	.	21.60	„ earth.	.	1
Water	.	9.24	„ water.	.	8
		<hr/>			
		100.00			

100 parts lose, at 212° F., 125 parts of water; 100 parts of the anhydrous salt contain 75.72 acid, and 24.28 baryta.

Carbazotate of Lime, obtained like the salt of baryta, forms flattened quadrangular prisms, very soluble in water, and detonating like the salt of potash.

“ *Carbazotate of Magnesia* forms very long indistinct needles, of a clear yellow colour; is very soluble, and detonates violently.

Carbazotate of Copper is prepared by decomposing sulphate of copper by carbazotate of baryta; it crystallizes with difficulty, the crystals being of a fine green colour; it is deliquescent; when heated, it is decomposed without explosion, and even without inflammation.

Carbazotate of Silver.—Carbazotic acid readily dissolves oxide of silver, when heated with it and water; and the solution, gradually evaporated, yields starry groups of fine acicular crystals of the colour and lustre of gold; the salt dissolves readily in water; when heated to a certain degree, it does not detonate, but fuses like gunpowder.

Proto-Carbazotate of Mercury is obtained in small yellow triangular crystals, by mixing boiling solutions of the carbazotate of potash or soda, and proto-nitrate of mercury. It requires more than 1200 parts of water for its solution: for its perfect purification, it should be heated with a solution of chloride of potassium, the insoluble portion separated whilst the liquid is hot, and the peculiar salt allowed to deposit as the temperature falls. When heated, it behaves like the salt of silver. It consists of 53.79 acid, and 46.21 protoxide of mercury per cent.

Carbazotate of Lead may be formed by decomposing a salt of lead by carbazotate of potash or soda; it is a yellow powder, but slightly soluble, and detonating by heat.

All these salts detonate much more powerfully when heated in close vessels, than when heated in the air; and it is curious to observe, that those with bases yielding oxygen most readily, are those which explode with least force. By heating some of the salts previously mixed with chloride of potassium, &c., to retard the action, it appeared that no carbonic oxide, but only carbonic acid and nitrogen were evolved during their decomposition by heat.

When indigo is acted on by dilute nitric acid, a peculiar acid, which appears perfectly distinct from the above, was obtained by Chevreul, and has been examined more in detail by Dr. Buff. It has by some been termed *Indigotic acid*.

To obtain it, nitric acid, of sp. grav. 1.285, was diluted with rather more than its weight of water, heated in a retort, and small portions of indigo in fine powder added as long as sensible effervescence was produced; a little water was added from time to time, to prevent the formation of carbazotic acid. The yellow liquid was separated, whilst hot, from the resinous matter, and by cooling deposited crystals of the acid of indigo. This was boiled with oxide of lead, filtered, and the salt present decomposed by sulphuric acid whilst hot; on cooling, the liquor deposited the acid of indigo in yellowish-white crystals; these were separated, dissolved in hot water, neutralized by carbonate of baryta, the solution concentrated, and allowed to cool; yellow acicular crystals of a barytic salt were obtained, which, being washed with cold water, dissolved in hot water, and decomposed by acids, gave acicular crystals of the acid of indigo, white as snow; they were collected, and washed upon a filter, and shrunk into a small space when dry, losing almost entirely their crystalline aspect.

This acid is white, having the lustre of silk; it has a weak acid, bitter taste, reddens litmus, dissolves in any quantity in boiling water or alcohol, forming colourless solutions, but requires 1000 parts of cold water for its solution. It is volatile, and, being heated in a tube, fuses and sublimes without decomposition. When the fused acid is cooled, it crystallizes in six-sided plates. In the air it burns with a bright flame, evolving much smoke. Nitric acid changes it into carbazotic acid. Neither chlorine gas, nor solution of chlorine, has any effect

upon it. It gives a blood-red colour to solutions of the persalts of iron.

When decomposed by heat and oxide of copper, it yields nitrogen and carbonic acid; the proportions of these gases in volume being 1 and 15. These are exactly the same proportions which, according to Mr. Crum and Dr. Buff, are given by pure indigo itself; so that the nitrogen and carbon are probably in the same relation both in indigo and the acid of indigo. The elements of the acid, according to three experiments, are as follows:—

Hydrogen	.	.	1.73	.	2.03	.	2.417
Carbon	.	.	46.34	.	48.21	.	46.244
Nitrogen	.	.	7.22	.	7.55	.	7.225
Oxygen	.	.	44.71	.	42.21	.	44.144

The acid of indigo combines with all bases, and has power to expel carbonic acid from carbonates. The salts have a yellow colour. When heated, they are decomposed without explosion. The proportional number of the acid, drawn from its combination with baryta, is 254.7; for 100 parts of the acid combine with 30.07 of baryta.

Prussian blue is frequently employed in calico-printing, the pattern being printed in an iron mordant, and rendered blue by passing it through an acidulated solution of ferro-cyanate of potassa. It has also lately been successfully used in dyeing wool. (RAYMOND, *Quarterly Journal*, N. S., viii. p. 427.)

Yellow. There are several dye stuffs employed in the production of yellows. A decoction of *Weld* (*Reseda Luteola*), with an aluminous mordant, gives a good yellow, which is rendered more brilliant by tartar, and by permuriate of tin.

The bark of the American oak (*Quercus Nigra*), or *Quercitron Bark*, also furnishes excellent yellows; it was first introduced into England by Dr. Bancroft, who has fully and philosophically detailed its various applications. (*Experimental Researches concerning the Philosophy of Permanent Colours*, &c., London, 1813.) The salts of alumina and of tin are the principal mordants employed both with wool and cotton.

Fustic wood, *sumach*, and *dyers' broom*, are also occasionally employed as sources of yellow colours.

Among the mineral yellows, sulphuret of arsenic and chro-

mate of lead have been occasionally employed in dyeing and calico-printing. (*Quarterly Journal*, xi. 392.)

Reds are chiefly produced from *madder*, the prepared root of the *Rubia Tinctorum*. The colouring matter is fixed by an aluminous mordant, assisted by galls and oil, but the process is very complex and circuitous. In Dr. Bancroft's work above quoted (vol. ii.) are full details upon this subject; and a perspicuous abstract of them will be found in Aikin's *Dictionary*, Art. DYEING.

Colin and Robiquet have obtained a peculiar crystallizable substance from madder, which they call *Alizarine*, derived from the term *Aliz-ari*, by which madder is known in the Levant. (*Ann. de Chim. et Phys.* xxxiv. 225.) There are several processes for its preparation, the simplest of which appears to be the following, suggested by Mr. Zenneck (*Quart. Journ. N. S.*, v. 198):—

Digest ten parts of finely-powdered madder with four parts of ether, in a close flask; the clear solution is to be distilled until the residue is thick like a syrup, and then dried upon plates in the open air, powdered, and sublimed.

The sublimation is to be effected in a watch-glass, or a metallic capsule, covered by a very low cone, on which the vapours are to be condensed; the layer of matter to be sublimed must be thin, and the distance through which the vapours have to pass as small as possible; a little cotton should be placed at the orifice in the summit of the condensing cone, and the heat applied moderate, especially at the commencement.

Alizarine, well sublimed, is in very brilliant, diaphanous, yellowish-red, acicular, quadrangular crystals; they are soft, flexible, heavier than water; have an acid taste, soften when heated, sublime at the temperature of boiling oil, and then occasion a peculiar aromatic odour. It is nearly insoluble in cold water. At common temperature, one part dissolves in 210 of alcohol, and in 160 of ether. It combines with and dissolves in alkalis, forming violet solutions; and, in fact, has all the properties of an acid. It even passes to the positive pole of the voltaic pile; and when boiled with metallic zinc, causes its oxidation, and then unites with it; 100 parts combine with and saturate 350 parts of oxide of lead; so that it has a greater

saturating power than oxalic acid. Its composition *per cent.* is given as 18 carbon, 20 hydrogen, and 62 oxygen.

Brazil wood, *safflower*, and *logwood* are occasionally employed as red or pink dye stuffs, but they only give fugitive colours. Effective lilac dyes are produceable, according to Dr. Mac Culloch, from the berries of the Portugal laurel, and from the black currant after the juice has been expressed. (*Quarterly Journal, N. S.*, v. 294.)

Scarlet is produced exclusively by the colouring matter of the *cochineal*, a small insect brought from Mexico, where it is found upon different species of the *Opuntia*. The nature of this colouring matter has been investigated by MM. Pelletier and Caventou; it is united in the insect with a peculiar animal matter, fat, and some saline substances; they separated it by exposing a strong alcoholic tincture of cochineal to spontaneous evaporation; it deposited a crystalline matter, which was redissolved in alcohol and the solution mixed with its bulk of sulphuric ether; this caused it in a few days to deposit the pure colouring principle, which they call *Carminium*: Dr. John has proposed for it the term *Coccinellin*. This substance is fusible at about 120°, very soluble in water, less so in alcohol, and insoluble in ether; the acids change its colour from purple to pale red or yellow: the alkalis render it violet; and its colour is impaired by most saline solutions. It readily combines with alumina, forming a beautiful *lake* or *carmine*. He obtained from 100 parts of cochineal, 50 of coccinellin, 24.5 gelatine and mucous matter, 10 waxy fat, 14 membrane, 1.5 saline matters.

The colouring matter of cochineal is fixed upon wool by nitromuriate of tin and tartar, by which scarlets are produced, and alum changes the scarlet to crimson. Cotton and linen are very rarely dyed with cochineal, for, independent of its great expense, the colours are little superior to those given by madder.

Buff and *Fawn colour* are produced in a variety of ways. *Walnut-husks* and *Sumach*, with alum mordants, give durable colours of this description, which are rendered *Drab*, or *Grey*, by a very little iron.

Green is obtained on woollen cloth, by passing it through the green indigo vat, and then dyeing it as for simple yellows,

the relative proportion of the blue and yellow being adjusted to the intended intensity of the green. Silk is first dyed yellow, and afterwards blued with indigo. *Saxon green* is done by dyeing yellow upon a Saxon blue ground. A solution of verdigris in vinegar is sometimes used to produce a delicate green: pearlash is added before it is used, and the cotton, previously impregnated with the alum mordant, is then passed through the mixture.

Besides the above, an infinite variety of *compound colours* are formed, by mixtures of the simpler tints, and of the mordants; but as my object is merely to give a general idea of the principles of the art of dyeing, I must refer the reader for practical details to the works expressly upon the subject, and more especially to Dr. Bancroft's *Treatise* already quoted.

Calico-printing is a more refined and difficult branch of the art of dyeing. In this process adjective colours are almost always employed. The mordants, the principal of which are acetate of alumina, and acetate of iron, are first applied to the calico by means of wooden blocks or copper-plates, upon which the requisite patterns are engraved. The stuff is then passed through the colouring-bath, and afterwards exposed on the bleaching-ground, or washed. The colour flies from those parts which have not received the mordant, and is permanently retained on those parts only, to which the basis has been applied: variety of colours is produced by employing various mordants, and different colouring materials.

White spots upon a dark ground are sometimes produced by covering the parts with wax, pipe-clay, or other materials, which prevent the contact of the colour; or citric acid, thickened with gum, is applied like a mordant with the block or plate, which prevents the retention of the colour. Sometimes the colour is discharged in places by the application of chlorine, a process well illustrated in what are called *Bandana* handkerchiefs, of which an account will be found, by Dr. Ure, in the fifteenth volume of the *Quarterly Journal*.

Section XII. WAX.

THIS principle exists in many plants ; it may be obtained by bruising and boiling them in water : the wax separates and concretes on cooling.

The berries of the *Myrica cerifera*, and the leaves and stem of the *Ceroxylon*, afford considerable quantities of wax by this process. (BOSTOCK, NICHOLSON'S *Journal*, vol. iv., BRANDE, *Phil. Trans.*, 1811.) The glossy varnish upon the upper surface of the leaves of many trees is of a similar nature ; and though there are shades of difference, these varieties of wax possess the essential properties of that formed by the bee : indeed, it was formerly supposed that bees merely collected the wax already formed by the vegetable, but Huber's experiments show that the insect has the power of transmuting sugar into wax, and that it is in fact a secretion.

Pure wax (bleached bees'-wax*) is colourless and insipid ; its specific gravity is about .96 : it is insoluble in water, and fusible at a temperature of about 150° ; at a higher temperature it is converted into vapour, and may be distilled with little other change than the production of a small portion of stearic acid, and at a red heat it burns in the contact of air with a bright flame. It is sparingly soluble in boiling alcohol and ether, and is deposited as the solutions cool. Twenty parts of boiling alcohol dissolve about one of bees'-wax, of which not more than one-fifth is retained at the temperature of 60°, and this is thrown down by the addition of water. Cold ether appears without action on wax, but boiling ether takes up about one-tenth of its weight, and deposits nearly the whole on cooling. The fixed oils, when assisted by heat, readily dissolve it, and form a compound of variable consistenc y, which is the basis of *cerates* and *ointments*. Some of the volatile oils also dissolve wax, when aided by heat. It is soluble in the fixed alkalis, forming imperfect soapy compounds of very difficult solubility,

* The bleaching of bees'-wax is effected by exposing it in thin ribands upon the bleaching-ground. It may be whitened by chlorine, but wax so bleached never burns well ; it smells of, and appears to contain, chlorine.

and from which the acids separate the wax in an unaltered state. The acids, at common temperatures, scarcely act upon wax; hence the advantage of *wax-lute* for the retention of corrosive vapours. At the fusing point of wax it combines with sulphuric acid, and the solution congeals on cooling. Muriatic acid has no action upon it, and nitric acid, after long boiling, very slowly converts a portion of it into oxalic acid.

When myrtle-wax is digested in boiling alcohol, it affords, according to Dr. John, a soluble and insoluble portion; he has called the former *cerin*, the latter *myricin*. Cerin is insoluble in water and in cold alcohol and ether, but dissolves in those liquids when heated. Myricin is insoluble, under all circumstances, in alcohol and ether.

The term *cerine* has also been applied by Chevreul to a principle resembling wax, which he separated from cork; it is less fusible than wax, more soluble in alcohol, and partly converted into oxalic acid, by the action of nitric acid.

Bees'-wax has been analyzed by Gay-Lussac and by Dr. Ure, with the following results:—

	Gay Lussac.		Ure.
Carbon . . .	81.784	. . .	80.60
Hydrogen . . .	12.672	. . .	11.37
Oxygen . . .	5.541	. . .	7.94
	<hr/> 100.		<hr/> 100.

From which it is not improbable that wax is a compound of

13 proportionals of carbon	•	(6 × 13)	78
12 „ hydrogen	•	(1 × 12)	12
1 „ oxygen	•	.	8

numbers which are equivalent to

12 proportionals of protocarburet of hydrogen,	
1 „ carbonic oxide,	

Section XIII. FIXED OIL.

FIXED oil is generally obtained by pressure from certain seeds, such as the almond, linseed, and many others, and from the olive*. The specific gravity of the fixed oils is below that of water, varying from 918 to 936. They are viscid; insipid, or nearly so; and generally congeal at a temperature not so low as that required to freeze water, though a few remain liquid at very low temperatures. This is the case with linseed oil. A few of them are solid at the ordinary temperatures, and have been called *vegetable butters*†. They are insoluble in water, but by the aid of mucilage may be diffused through it, forming *emulsions*. They are, for the most part, sparingly soluble in alcohol and ether, though castor-oil dissolves in any quantity in those fluids.—BRANDE, *Phil. Trans.*, 1811.

Olive oil is sometimes adulterated with that of certain seeds,

* The fixed oils are generally divided into *fat* and *drying* oils. Of the former, those in common use are olive oil, almond oil, rape oil, and castor oil; of the latter, linseed oil, walnut oil, poppy-seed oil, and hempseed oil.

The expressed oil of the seeds of the *croton tiglium* has lately been reintroduced into medicine as a drastic purge. It has a brown or yellow colour, an acrid taste, and is operative in doses not exceeding a single drop: the oil, however, as met with in commerce, varies much in activity. When the seeds are digested in ether we obtain, according to Nimmo, 60 *per cent.* of their weight of oil, of which two-thirds are soluble in alcohol and purgative; one-third is bland and inert. The acrid principle of the croton seed appears to be acid, and has been termed, by Pelletier and Caventou, *Iutrophic Acid*, from erroneously supposing the seeds to be the produce of the *iatropha curcas*. Brandes has since examined the acid, and calls it *Crotonic Acid*. In the oil of the seeds of the *Veratrum Sabadilla*, Pelletier and Caventou have also detected a peculiar acid, which they call *Cevadic Acid*.

† The principal vegetable butters are cocoa-nut oil, palm oil, and nutmeg oil. The latter is largely prepared in Holland, and occasionally used in medicine. According to Schrader, 16 ounces of the concrete expressed oil of nutmeg contain 7 of hard concrete oil, 8½ yellow butyraceous oil, and ½ volatile oil. Cold alcohol dissolves the volatile and the soft oil, and leaves the harder oil. When nutmeg oil is boiled in four parts of alcohol, it is entirely dissolved, and the harder fatty portion is deposited as the solution cools. Marrow, or common fat, scented by a little oil and powder of nutmeg, and coloured by annatto, is sometimes substituted for this oil: the fraud is detected by the insolubility of this artificial mixture in four parts of boiling alcohol.

which may be detected by the action of nitrate of mercury. For this purpose, 6 parts of mercury are dissolved without heat in 7.5 parts of nitric acid, specific gravity 1.36; this solution, shaken with olive oil, becomes solid in a few hours; but if sophisticated with oil of grains, it does not solidify it.

If oil, which has been congealed by cold, be submitted to pressure between folds of bibulous paper, a dry, concrete, fatty matter is obtained, which Chevreul has called *Stearine*: the paper absorbs a fluid matter, which does not congeal at a much lower temperature, and which, though it does not become rancid, acquires viscosity by exposure to air. This fluid part he has called *Elaine*. The relative proportions of these principles differ in the different oils.—*Annales de Chimie*, tom. xciii. xciv.—See *Animal Oils*.

These oils cannot be volatilized without decomposition, which takes place at a temperature of about 600°, and water is copiously formed, attended by the separation of carbonaceous matter, which causes the oil to blacken and grow thick; a portion of acetic acid is also at the same time formed. If the vapour be collected, it is found acrid, sour, and empyreumatic; it was formerly employed in pharmacy, under the name of *philosophers' oil*; and as it was often obtained by steeping a brick in oil, and submitting it to distillation, it was also called *oil of bricks*. Passed through a red-hot tube, the fixed oils furnish a very large proportion of carburetted hydrogen gas; and when burned in the wicks of lamps they suffer a similar decomposition, and water and carbonic acid are the products of their combustion. The results of the distillation of the fixed oils have been examined by Dupuy, and by Bussy and Lecanu. The former subjected olive oil to its boiling point in a distillatory apparatus; white vapours passed over, which condensed into a liquid that became concrete on cooling, a fluid empyreumatic oil was also formed, and there remained a scanty portion of charcoal in the retort. The concrete portion was a mixture of oleic and margaric acids with a peculiar acrid, volatile principle; sebatic acid, and another acid matter, were also formed.

Bussy and Lecanu (*Ann. de Chim. et Phys.*, xxxi., xxxiii., and xxxiv.) distilled poppy oil at a temperature a little below 400°; it exhaled an acrid odour, and yielded about one-third its weight of an oil which concreted on cooling, (a mixture chiefly

of margaric, oleic, and benzoic acids.) This was succeeded by a liquid oil, which became turbid on exposure to air, was little soluble in alcohol, and not acted upon by the alkalis. Lastly, when the retort became red-hot, a solid of the colour of realgar sublimed, which was without smell or taste, fusible in boiling water, and soluble in boiling alcohol and cold ether. Carburated hydrogen, carbonic oxide, and carbonic acid, were also produced.

The greater number of the fixed oils undergo little other change by exposure to air than that of becoming somewhat more viscid, and acquiring a degree of rancidity. In this state they contain free acid, and reddened vegetable blues. Some few, such as linseed and nut oil, and the oils of the poppy and hempseed, become covered with a pellicle, and, when thinly spread upon a surface, instead of remaining greasy, become hard and resinous; these are termed *drying oils*, and their drying quality is much improved by boiling them upon a small quantity of litharge. The quantity of oxygen absorbed by some of the oils is very considerable. Saussure exposed nut-oil, for eight months, to oxygen gas; at first the absorption was trifling, but in the course of ten days it had taken up 60 times its volume, and in three months 145 times its volume, the absorption being most rapid in warm weather. It is well known that cotton and hemp, soiled with certain oils, are liable to spontaneous ignition; and Berzelius plausibly refers the phenomenon to the heat excited by the absorption of oxygen. No water was produced in Saussure's experiments, but carbonic acid was evolved, and the oil lost its greasy character and assumed a gelatinous appearance. (See some observations on the spontaneous combustion of cotton goods, by Dr. M. HALL, *Quarterly Journal, O. S.*, v. 367.)

The drying oils, and especially nut oil, form the basis of *printers' ink*, the history of which will be found in LEWIS'S *Phil. Commerce of the Arts*. The oil is heated and set fire to, and, after having been suffered to burn for half an hour, is extinguished, and boiled till it acquires a due consistency; in this state it is called *Varnish*, and is viscid, tenacious, and easily miscible with fresh oil, or with oil of turpentine, by which it is properly thinned, and afterwards mixed with about one-eighth part of lamp-black.

The alkalis readily combine with the fixed oils, and form white compounds called *Soap*. Of these the most important is the *soap of soda*, which is thus made : Five parts of barilla are mixed with one of lime and a proper quantity of water. In this way a *ley*, or solution of caustic soda, is obtained, which is boiled in an iron pot with six parts of oil, till the soap separates, which is accelerated by the addition of common salt ; it is then suffered more perfectly to congeal, and in a few days becomes hard enough to cut into forms. (AIKIN'S *Dictionary*—Art. SOAP.) The best soaps are made with olive oil and soda ; in this country animal fat is usually employed for the common soaps, to which resin and some other substances are occasionally added. *Soft Soap* is a compound of potassa with some of the common oils ; even fish oil is often used.

Among the curious products of the process of saponification, which have been so elaborately explained by Chevreul (see *Animal Oils*), is one discovered by Scheele, and called by him the *sweet principle* ; it has since been termed *glycerine*. It may be obtained by saturating the alkaline mother liquor, from which the soap has congealed, by sulphuric acid, adding a little carbonate of baryta to remove any slight excess of the acid, filtering, and evaporating to the consistency of thin syrup, to which alcohol is then added, which dissolves the glycerine and leaves the alkaline sulphate. Glycerine is not crystallizable ; it has a pure sweet flavour, and cannot be deprived of water without decomposition. When distilled, a portion passes over unaltered. Heated in the air it burns with a blue flame. It is very difficult of conversion into oxalic acid by the action of nitric acid, and has very little tendency to fermentation.

Soap furnishes a milky solution with water. It dissolves in alcohol, and the solution, if concentrated, is of a gelatinous consistency. By carefully distilling off the alcohol, a *transparent soap* is obtained.

The acids and the greater number of salts decompose soap, forming, in most cases, a compound of difficult solubility ; hence *hard waters* are unfit for washing, in consequence of containing sulphate of lime ; hence, also, the alcoholic solution of soap is useful as a test for ascertaining the fitness of water for this purpose, which, if it becomes very turbid, cannot in general be used for washing.

When soaps are decomposed by the acids, the oil which they contain is found to have undergone a change, the history of which will be noticed under the head of *Animal Oils*.

The fixed oils readily combine with hydrated oxide of lead (HENNEL, *Quarterly Journal*), when aided by heat, forming the compound usually termed *plaster*; with the oxides of mercury and bismuth they produce very similar combinations, and are also capable of dissolving white arsenic in large proportion. They also dissolve sulphur and phosphorus, and the solutions sometimes spontaneously deposit those substances in the form of crystals.

Chlorine effects a singular change in some of the fixed oils, converting them into a substance resembling hard tallow or wax. This is especially the case with castor-oil. Muriatic acid is at the same time formed. Gaultier de Claubry has described the action of the acids upon these oils in a Memoir published in the *Journal de Physique* (1815).

The ultimate components of olive oil, as given by Gay-Lussac and Thenard, are

Carbon	77.21
Oxygen	9.43
Hydrogen	13.36
						<hr/>
						100

These elements may be supposed to correspond to

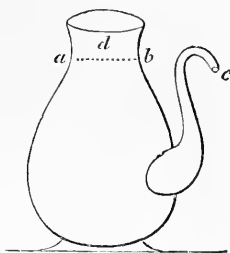
10	proportionals of carbon	.	(6 × 10) =	60	..	76
11	„ hydrogen	.	(1 × 11) =	11	..	14
1	„ oxygen	.	.	=	8	.. 10
				<hr/>		<hr/>
				79		100

or to 10 proportionals of protocarburet of hydrogen and 1 of water.

Section XIV. VOLATILE OILS.

THESE oils are generally obtained by distilling the plants which afford them with water in common stills; the water and oil pass over together, and are collected in the *Italian recipient* shown in the following cut, in which the water, having reached the

level *a b*, runs off by the pipe *c*, and the oil being generally lighter than water, floats upon its surface in the space *d*. The whole contents of the recipient are then poured into a funnel, the tube of which is closed with the finger; and when the oil has collected upon the surface, the water is suffered to run from it, and the oil transferred into a bottle. The distilled water, being saturated with the oil, should be retained for a repetition of the distillation. The produce of oil is sometimes increased, by adding salt to the water in the still, so as to elevate its boiling point a few degrees.



Some of the volatile oils are obtained by expression, such as those of *lemon*, *orange*, and *bergamot*, which are contained in distinct vesicles in the rind of those fruits.

The volatile oils vary considerably in specific gravity, as shown by the following Table:—

Oil of Sassafras	.	.	.	1.094
„ Cinnamon	.	.	.	1.035
„ Cloves	.	.	.	1.034
„ Fennel	.	.	.	997
„ Dill	.	.	.	994
„ Pennyroyal	.	.	.	978
„ Cummin	.	.	.	975
„ Mint	.	.	.	975
„ Nutmegs	.	.	.	948
„ Tansy	.	.	.	946
„ Caraway	.	.	.	940
„ Origanum	.	.	.	940
„ Spike	.	.	.	936
„ Rosemary	.	.	.	934
„ Juniper	.	.	.	911
„ Oranges	.	.	.	888
„ Turpentine	.	.	.	872

The volatile oils have a penetrating odour and taste, and are generally of a yellowish colour; they are for the most part very soluble in alcohol, and very sparingly soluble in water; these solutions constitute *perfumed essences* and *distilled waters*. The latter are principally employed in pharmacy, and the former as perfumes.

When pure, they pass into vapour at a temperature some-

what above that of 212° , but when distilled with water, they pass over at its boiling point. They are very inflammable, and water and carbonic acid are the results of their perfect combustion. As many of these oils bear a very high price, they are not unfrequently adulterated with alcohol and fixed oils. The former addition is rendered evident by the action of water; the latter, by the greasy spot which they leave on paper, and which does not evaporate when gently heated. By long keeping, some of the essential oils are concentered into a substance resembling spermaceti; this is especially the case with the ottar of rose, and appears connected with the destruction of its odoriferous principle. When oil of aniseed is kept for many years it also loses its odour, and becomes entirely solid. Other oils become resinous by age. (MAC CULLOCH, *Quarterly Journal*, N. S., v. 291.)

The volatile oils absorb oxygen, when long exposed to it, and become thick and resinous. Nitric and sulphuric acids rapidly decompose the volatile oils: a mixture of four parts of nitric, and one of sulphuric acid, poured into a small quantity of oil of turpentine, produces instant inflammation. They absorb chlorine, and muriatic acid is produced, along with a peculiar substance, in some cases not unlike camphor. Iodine produces changes somewhat analogous. Muriatic acid combines with several of them, and forms a crystallizable compound which has been compared to camphor.

The relative quantity of essential oils, furnished from different materials, is liable to much variation; the following are the products of 1 cwt. of the different vegetable substances:—

		Ounces.	
Juniper-berries (common)	.	4	to 5
„ (fine Italian)	.	7	„ 8
Aniseed (common)	.	32	„ 36
„ (finest)	.	36	„ 38
		lbs.	oz.
Caraways	from	3	12
Dill-seed	„	2	0
Cloves	„	18	0
Pimento	„	2	0
Fennel-seed	.	.	2 0
Leaves of the <i>Juniperus Sabina</i>	.	.	0 14

Oil of turpentine is one of the most important of these oils, in consequence of its numerous applications in the arts, espe-

cially in the manufacture of paints and varnishes. It is obtained by distilling turpentine with water, with the vapour of which it readily passes over at 212° , though its boiling point exceeds 314° . It is very sparingly soluble in alcohol. By exposure to air a part of it is converted into resinous matter, and a part into a peculiar acid matter, which, when distilled, deposits a crystallizable substance, upon exposure to cold. (*Ann. de Chim. et Phys.*, xxxi., 442.) In consequence of the great inflammability of oil of turpentine, it is highly dangerous when kept in quantities. If preserved in wooden vessels they are very apt to leak, hence the necessity of placing them in another cask, surrounded by water. In common oil of turpentine Dr. Ure found 82.35 carbon, 9.80 hydrogen, 7.85 oxygen: when purified by alcohol, the specific gravity of this oil was reduced from 888 to 878; it then appeared to be a binary compound of carbon and hydrogen, nearly resembling naphtha in composition.

Section XV. CAMPHOR.

THIS substance in many respects resembles the essential oils; like them it is volatile, inflammable, soluble in alcohol, and sparingly soluble in water.

In its ordinary state it is white, semi-transparent, and concrete. Its specific gravity is .98. It fuses at about 300° , in close vessels. It dissolves in the fixed and volatile oils. It is scarcely acted upon by the alkalis; some of the acids dissolve, others decompose it.—HATCHETT, *Phil. Transactions*, 1805. CHEVREUL, *Annales de Chimie*, lxxiii.

If mixed with bole or powdered clay, and repeatedly distilled, it is almost entirely converted into a liquid, having the characters of essential oil.

The camphor of commerce is obtained from the *Laurus Camphora*, and comes chiefly from Japan. It is originally separated by distillation, and subsequently purified in Europe in a subliming vessel somewhat of the shape of a turnip, from which the cakes of camphor derive their form.

When camphor is repeatedly distilled with nitric acid, it is

converted into *camphoric acid*. For this purpose, four ounces of camphor, reduced to powder by triturating it with a few drops of spirit of wine, may be introduced into a two-quart tubulated retort, placed in a sand heat; pour upon it thirty ounces of common nitric acid, and proceed to slow distillation. When two-thirds of the acid have passed over, return it into the retort and distil as before, repeating the operation twice more; after which, as the liquor cools, a quantity of crystals of camphoric acid are deposited, which are to be washed and dried. This acid assumes the form of plumose crystals, soluble in about 100 parts of water at 60° , and in rather more than 1 part of alcohol. Its taste is acid, and somewhat acrid, and it has an aromatic odour. Exposed to heat, it sublimes unaltered. It combines with the salifiable bases, constituting a class of salts called *Camphorates*.

Camphorate of Ammonia is with difficulty crystallized; it is sparingly soluble in water, but more copiously in alcohol.

Camphorate of Potassa forms hexagonal crystals, soluble in about 100 parts of water at 60° , and in 25 parts at 212° . Its alcoholic solution burns with a blue flame.

Camphorate of Soda is possessed nearly of the same properties as the preceding.

Camphorate of Lime is nearly insoluble in water and alcohol.

Camphorate of Baryta forms difficultly soluble lamellar crystals.—BOUILLON LAGRANGE, *Annales de Chimie*, xxvii.

When a current of muriatic acid gas is passed through oil of turpentine, it deposits a concrete substance, which has been called *artificial camphor*, and the weight of which amounts to about one-half of the oil employed. When purified by sublimation with a little quicklime, it is rendered pure and white. It is lighter than water, sublimes without decomposition, burns like camphor, and in smell resembles a mixture of camphor and turpentine. (THENARD, *Mémoires d'Arcueil*, tom. ii.) By the action of zinc it affords chloride of zinc, and the oil is evolved little altered.

Camphor dissolves in sulphuric acid, forming a brown solution, from which it is at first precipitated, unaltered, by water. Sulphurous acid is afterwards evolved, the solution becomes black and thick, and, after some days, affords a brown coagulum on the addition of water, and smells fragrant and peculiar.

On distilling the diluted liquor, water and a yellow oil pass over, a little sulphurous acid is then disengaged, and a black matter remains in the retort, which, when digested in alcohol, affords a portion of soluble matter having some of the properties of artificial tannin.—HATCHETT, *Phil. Trans.* 1805.

According to Dr. Ure, the following are the ultimate components of camphor:—

Carbon	°	78.02
Hydrogen	11.58
Oxygen	10.40
						<hr/>
						100

These numbers may be construed into 10 proportionals of carbon, 9 of hydrogen, and 1 of oxygen; or,

Carbon	60
Hydrogen	9
Oxygen	8
						<hr/>
						77

Section XVI. RESINS.

RESINS are substances which exude from many trees, either from natural fissures or artificial wounds. They are of much use in the arts, and their solutions in alcohol form the bases of different varnishes*.

Common resin is obtained by distilling the exudation of different species of fir: *oil of turpentine* passes over, and the resin remains behind. It may be taken as a perfect example of resin, and is possessed of the following properties: It is solid, brittle, a little heavier than water, its specific gravity being 1080; it acquires negative electricity when rubbed. It is extremely inflammable, and during its combustion throws off a large quantity of finely divided carbon, which, when collected, is known under the name of *lamp black*. It softens at a temperature below that of boiling water; at 256° it becomes perfectly liquid, loses a portion of water, and concretes into the transparent dark-brown resin called *Colophony*. It

* A detailed account of the manufacture of varnishes would be irrelevant to this work: there is an excellent article on the subject in Aikin's *Chemical Dictionary*.

has scarcely any taste or smell ; is insoluble in water ; readily soluble in alcohol, which takes up about one-third its weight, and becomes milky upon the addition of water. Resin is soluble in the caustic alkalis ; the solution is saponaceous, and, when mixed with an acid, the resin separates, scarcely altered in its properties. Muriatic and acetic acids dissolve it without much change * : so, in the first instance, does nitric acid ; but if the solution be digested, the resin is gradually converted into artificial tan ; in this case, no oxalic acid is formed,—a character which distinguishes the resins.

The ultimate analyses of common resin are much at variance. The following are the results given by Gay-Lussac and Ure:—

Carbon	.	.	75.944	.	.	75.00
Oxygen	.	.	13.337	.	.	12.50
Hydrogen	.	.	10.719	.	.	12.50

A few of the resins derive odour from containing essential oil ; some afford benzoic acid when heated, and these have been termed *balsams* ; such as *tolu balsam* and *benzoin*. The term balsam is also applied to certain liquid compounds of resin and essential oil ; such as *balsam of Copaiva*, *balsam of Mecca*, &c., and to which, in *Peruvian balsam*, benzoic acid is super-added.

Copal, *mastich*, and a few other resins, are very difficultly soluble in alcohol, and contain a substance somewhat analogous to caoutchouc, which remains in the form of a viscid matter after the resinous portion has been separated by alcohol. Copal requires peculiar management to effect its solution in alcohol. A piece suspended in the vapour of boiling alcohol is gradually softened, and, as it drops down, dissolves in the alcohol ; camphor also accelerates its solution both in alcohol and in oil of turpentine. The most useful copal varnishes are those in which it is dissolved in linseed oil and turpentine.

Guaiacum is characterized by the singular changes of colour, which its alcoholic solution suffers when exposed to the action of nitric acid. (*Phil. Trans.* 1811.) Guaiacum is also rendered blue by the gluten of wheat, but its colour is not changed by starch ; the intensity of the blue colour is said to be pro-

* The properties of the resins have been very ably investigated by Mr. Hatchett, the details of whose researches will be found in his communications to the Royal Society, printed in the *Philosophical Transactions* for 1804, 1805, 1806.

portional to the quantity of gluten present in flour. (TADDEI, *Giornale di Fisica*, i. 168. *Quarterly Journal*, viii. 376.) M. Pagenstecher has employed tincture of guaiacum, in conjunction with prussic acid, as a test of the presence of copper. (*Quarterly Journal*, x. 182.)

Lac is a substance formed by an insect, and deposited on different species of trees, chiefly in the East Indies. The various kinds of lac distinguished in commerce are *stick-lac*, which is the substance in its natural state, investing the small twigs of the tree; *seed-lac*, which is the same broken off, and which, when melted, is called *shell-lac*. These substances have been examined by Mr. Hatchett*. The following table exhibits their component parts. (*Phil. Trans.* 1804.)

	Stick-lac.		Seed-lac.		Shell-lac.
Resin . . .	68	. . .	88.5	. . .	90.9
Colouring matter	10	. . .	2.5	. . .	0.5
Wax . . .	6	. . .	4.5	. . .	4.0
Gluten . . .	5.5	. . .	2.0	. . .	2.8
Foreign bodies .	6.5	. . .	—	. . .	—
Loss . . .	4.0	. . .	2.5	. . .	1.8
	<hr/> 100		<hr/> 100		<hr/> 100

Dr. John has announced the presence of a peculiar acid in stick-lac, which he has called *laccic acid*. The lac was digested in water, the solution evaporated, and the residue digested in alcohol: the alcoholic solution was evaporated to dryness, and its residue digested in ether. The evaporation of the etheric solution leaves a yellow matter, which, being again dissolved in alcohol, and the solution mixed with water, deposits a little resin, and leaves laccic acid in solution, which, upon the addition of acetate of lead, gives a precipitate of *laccate of lead*; the latter compound, by cautious decomposition by sulphuric acid, affords the laccic acid.

Laccic acid is crystallizable, of a yellow colour, a sour taste, and soluble in water, alcohol, and ether. With potassa, soda, and lime, it forms deliquescent soluble salts; with lead and mercury it produces white insoluble compounds; it occasions no precipitate in the nitrates of baryta and silver. (THOMSON'S *System*, ii. 177.)

* Dr. Pearson obtained a peculiar acid from a substance called *white lac*, from Madras. He has called it *laccic acid*.—*Phil. Trans.* 1794.

Gum resins are natural combinations of gum and resin, they are consequently only partially soluble in water and in alcohol; they readily dissolve in alkaline solutions when assisted by heat; and the acids act upon them nearly as upon the resins. *Ammoniacum*, *gamboge*, *assafœtida*, and *olibanum*, may be taken as examples of gum resins.

Amber is a substance which, in some of its properties, resembles resin; it is, however, very sparingly soluble in alcohol, and difficultly soluble in the alkalis. Its specific gravity is 1.065. When submitted to distillation, it furnishes an acid sublimate, which has received the name of *succinic acid*. To obtain this acid in the largest quantity, M. Julien recommends coarsely powdering the amber and mixing with it, previous to distillation, one-twelfth part of sulphuric acid diluted with an equal weight of water; about twice as much acid, he says, will thus be produced as when the amber is merely heated alone. (*Annals of Phil.* ii. 76.) When purified by repeated solutions and crystallization, *succinic acid* possesses the following properties:—

It forms yellowish prismatic crystals soluble in 24 parts of water at 60°, very soluble in alcohol, and of a slightly acid and nauseous taste; it is fusible and volatile when heated, but not without partial decomposition. 10 lbs. of amber yield about 3 ounces of purified succinic acid. Along with the succinic acid there distils over a quantity of volatile oil, of a light brown colour, used in pharmacy under the name of *Oil of Amber*, and amounting to about one-third in weight of the amber used.

The perfect purification of succinic acid is attended with some difficulty; Richter recommends the saturation of the sublimate with potassa, and ebullition with powdered charcoal; the solution is then filtered, and nitrate of lead added; the resulting insoluble succinate of lead is decomposed by the requisite addition of dilute sulphuric acid, and the solution of pure succinic acid thus obtained, being carefully evaporated, affords colourless prismatic crystals of the pure acid.

Succinate of Ammonia forms acicular crystals, which sublime when cautiously heated. Its solution has been used as a test for iron, the peroxide of which it throws down from its neutral solutions in the form of a reddish brown precipitate.

Succinate of Potassa is a very soluble deliquescent salt, crystallizable with difficulty in small prisms.

Succinate of Soda forms transparent four and six-sided prisms, considerably less soluble than the preceding, and permanent in the air.

Succinate of Lime forms permanent and difficultly soluble crystals.

Succinate of Baryta is formed by adding succinate of ammonia to muriate of baryta. A portion is thrown down in a pulverulent form, and a part, in small crystalline grains. —BERGMAN.

Succinate of Strontia may be formed as the preceding, and presents similar properties. It burns with a fine red flame.

Succinate of Magnesia is deliquescent and uncrystallizable.

Succinate of Manganese has been examined by Dr. John. (GEHLEN'S *Journal*, iy.) It is crystallizable, and of a slight red tinge; it consists of 30.27 protoxide of manganese + 69.73 acid and water. The theoretical constitution of succinate of manganese is

46.7 acid
36 oxide

so that the above salt is probably a bisuccinate.

Succinate of Iron.—The *protosuccinate* is crystallizable and soluble; the *persuccinate* is insoluble, and is thrown down in the form of a brownish red flaky precipitate from solutions of the peroxide of iron. This salt has been proposed as a means of separating iron in analysis, but is quite inapplicable in the greater number of cases.

Succinate of Zinc furnishes long slender crystals, which have not been examined.

Succinate of Tin.—The succinic acid dissolves protoxide of tin, and forms with it thin broad transparent crystals.

Succinate of Copper.—There appear to be two varieties of this salt, a supersuccinate and a subsuccinate. (For details respecting several of the succinates, the reader is referred to WENZEL'S *Lehre der Verwandtschaft der Körper*; and to GREN, *Handbuch*, iii. 19.)

Succinate of Lead.—When succinic acid, or succinate of

ammonia, is added to acetate of lead, a white precipitate of succinate of lead falls, composed, according to Berzelius, of

Succinic acid	30.9
Protoxide of lead	69.1
						<hr/>
						100.

These numbers give 50 as the representative of succinic acid; and, considering the succinate of lead as composed of 1 proportional of each of its components, it will consist of

Succinic acid	50
Protoxide of lead	112
						<hr/>
						162

The remaining succinates are not of sufficient importance to require enumeration.

The ultimate composition of succinic acid is, according to Berzelius,

Carbon	.	.	47.600	= 4 proportionals	24
Hydrogen	.	.	4.512	= 2	2
Oxygen	.	.	47.888	= 3	24
			<hr/>		<hr/>
			100.		50

It will appear, by reference to acetic acid, that these are the components and the equivalents of that acid; but ultimate analysis has not yet attained that perfection which enables us to place implicit confidence in its results.

Section XVII. BITUMENS, COAL, &c.

BITUMENS are fossil substances, bearing considerable resemblance to oily and resinous bodies. The chemical habitudes of several of these substances have been ably investigated by Mr. Hatchett. (*Phil. Trans.* 1804.) The following are the principal varieties:—

a. Naphtha has already been adverted to as a binary compound of carbon and hydrogen; it is a pungent, odoriferous, oily liquid, either colourless or of a pale brown tint, found

upon the borders of the Caspian Sea, and in certain springs in Italy. It is considerably lighter than water, its specific gravity varying from 708 to 850; it is volatile, and highly inflammable. When pure, it appears to contain no oxygen, and hence is employed for the preservation of potassium, and the other highly oxidable metals. It consists, according to Saussure, of

Carbon	87.21
Hydrogen	12.79
							<hr/>
							100.

b. Petroleum has most of the properties of naphtha, but is less fluid, and darker coloured. In the countries where it abounds, it is employed for burning in lamps. By distillation, it affords a substance resembling naphtha, and mineral pitch or asphaltum remains in the retort.

c. Mineral Tar appears to be petroleum further inspissated. It is more viscid, and of a deeper colour.

d. Maltha, or *Mineral Pitch*, is a soft inflammable substance, heavier than water, and may be considered as derived from the exsiccation of mineral tar.

e. Asphaltum is found abundantly on the shores of the Dead Sea, in Albania, and in the island of Trinidad. Its colour is brown or black; it is heavier than water, and readily soluble in naphtha. Asphaltum was one of the materials used by the ancient Egyptians in embalming; hence termed *mumia mineralis*. At Babylon it was used for mortar. It dissolves in naphtha, and the solution forms a good varnish.

f. Elastic Bitumen, or *Mineral Caoutchouc*, is found only in the vicinity of Castleton in Derbyshire, and at Montrelais in France. It is fusible and inflammable, and when distilled *per se*, affords products corresponding to petroleum and asphaltum.

g. Mineral Adipocire, or *Hatchetine*, is a fatty matter found in the argillaceous iron ore of Merthyr: it is fusible at about 160° , and inodorous when cold, but of a slightly bituminous odour when heated, or after fusion.

The above substances are insoluble in water, and difficultly soluble in alcohol, with the exception of naphtha and petroleum, which are soluble in highly rectified alcohol.

h. Retinasphaltum is a substance which accompanies the

Bovey coal of Devonshire. I have also found it in some of the Staffordshire coal. It was first analyzed by Mr. Hatchett, who found it to consist of

55 Resin
41 Asphaltum
4 Earthy matter and loss.

i. Pit Coal. There are three chemical varieties of this important substance. The first, or *brown coal*, retains some remains of the vegetables from which it has originated. When heated, it exhales a bituminous odour, and burns with a clear flame. It is generally of a tough consistency, and yields, according to Mr. Hatchett, a portion of unaltered vegetable extract, and resin.

The second variety, or *black coal*, is the ordinary fuel of this country. It exhibits no traces of vegetable origin, and consists principally of bitumen and charcoal, in variable proportions. When exposed to heat, it swells, softens, and burns with a bright flame, leaving a small quantity of ashes. Many varieties, however, abound in earthy matter, and these produce copious cinders, and burn with a less intense heat.

The products of the destructive distillation of this kind of coal have been already described (Vol. I., p. 336). The residue is a hard, sonorous charcoal, termed *coke*, and containing the earthy ingredients of the coal.

The third variety, or *glance coal*, consists almost entirely of charcoal and earthy matter. It burns without flame, and, when distilled, produces scarcely any gaseous matter.

It is curious, that all the varieties of common coal contain nitrogen as one of their elements, and hence afford ammonia when subjected to destructive distillation. In consequence of the enormous quantities of pit coal distilled for the production of illuminating gas, a part of the commercial demand for ammoniacal salts is now supplied from that source.

k. Peat and Turf consist principally of the remains of vegetables, having undergone comparatively little change. They often contain bituminous wood, and branches, and trunks of trees.

l. Mellilite, or *Honeystone*, is a rare substance, found in the brown coal of Thuringia, and in Switzerland. It is of a honey-yellow colour, crystallized in octoëdra, and when analyzed by

Klaproth, was found to consist of alumina, combined with a peculiar body which has been called the *mellitic acid*.—KLAPROTH'S *Essays*, ii. 89. VAUQUELIN, *Annales de Chimie*, xxxvi. 203.

Section XVIII. VEGETABLE ACIDS.

THE following are the principal acids, which are found ready formed in vegetable products:—

1. Tartaric acid.
2. Oxalic acid.
3. Citric acid.
4. Malic acid.
5. Gallic acid.
6. Benzoic acid.

i. TARTARIC ACID.

This acid exists in several vegetable substances; it is one of the sour principles of many fruits, and is said to be abundant in the potato-apple. Tartaric acid is generally obtained from the *bitartrate of potassa*. Mix 100 parts of this salt in fine powder with 30 of powdered chalk, and gradually throw the mixture into 10 times its weight of boiling water: when the liquor has cooled, pour the whole upon a linen strainer, and wash the white powder which remains with cold water: this is a *tartrate of lime*; diffuse it through a sufficient quantity of water, add sulphuric acid equal in weight to the chalk employed, and occasionally stir the mixture during 24 hours; then filter, and carefully evaporate the liquor to about one-fourth its original bulk; filter again, and evaporate with much care nearly to dryness; redissolve the dry mass in about 6 times its weight of water—render it clear by filtration—evaporate slowly to the consistency of syrup—and set aside to crystallize. By two or three successive solutions and crystallizations, tartaric acid will be obtained in colourless crystals, soluble in 6 parts of water at 60°. They are rectangular prisms, terminated by dihedral or four-sided pyramidal sum-

mits. Their specific gravity is 1.6. They fuse at a temperature a little above 212° into a fluid which boils at 250° , and leaves a semi-transparent mass on cooling, which is slightly deliquescent. According to Berzelius, the crystals contain 11.25 *per cent.* of water. They dissolve in 5 parts of water at 60° , and are very soluble in water at 212° .

The following is by some recommended as a good process for the separation of tartaric acid. Mix 100 parts of finely powdered crystals of tartar with 40 of dry slacked lime, and add boiling water so as to form a liquor like cream; evaporate this to dryness, and digest the residue in water, which dissolves the potassa, and leaves tartrate of lime, to be decomposed by sulphuric acid as above: but Dr. Henry says, that in this process the potassa set at liberty prevents the precipitation of the tartrate of lime.

The aqueous solution of tartaric, in common with the other vegetable acids, soon becomes mouldy, and suffers decomposition. Boiled in nitric acid, tartaric acid is partly converted into oxalic acid.

When tartaric acid is submitted to destructive distillation, it affords a brown acid liquor which has been termed *pyrotartarous acid*. If this liquor, after having been passed through a wet filter to separate the oil, be saturated with carbonate of potassa, and evaporated to dryness, a saline mass is obtained, which, after having been twice or thrice redissolved and crystallized, is rendered free from empyreumatic matter. If this salt be distilled with sulphuric acid diluted with its weight of water, an acid liquor passes over, succeeded by a white sublimate of pure pyrotartaric acid. Rose, who has examined the properties and combinations of this body, considers it as a distinct acid; the *pyrotartrates of ammonia, potassa, soda, baryta, strontia, and lime*, are very soluble. The pyrotartaric acid occasions precipitates in acetate of lead, and in nitrate of mercury, and is thus, according to Rose, distinguished from tartaric acid, which only throws down the former;—but this is not a correct distinction.

In determining the ultimate composition of tartaric acid, Gay-Lussac and Thenard appear not to have excluded water of crystallization. The following are the analyses of Berzelius and Ure:—

	Berzelius.	Ure.
Carbon	35.98	31.42
Oxygen	60.28	65.82
Hydrogen	3.74	2.76

The most probable ultimate composition of dry tartaric acid appears to be that assigned to it by Berzelius, viz. :—

4 proportionals of carbon	24	36.36
5 " oxygen	40	60.61
2 " hydrogen	2	3.03
	<hr/>	<hr/>
	66	100

And, from the experiments of Berzelius and Prout*, the crystallized acid, deprived of adhering water, is a compound of

1 proportional of dry acid	=	66
1 " water	=	9
		<hr/>
		75

Tartaric acid combines with the metallic oxides, and produces a class of salts called *tartrates*, the composition of which will be obvious from the preceding datum. The presence of tartaric acid in metallic solutions frequently prevents their precipitation by alkalis and their carbonates.—*Quart. Journal*, xvi. 107. When tartaric acid is fused with five or six parts of caustic potassa, it is converted into oxalic acid.—(GAY-LUSSAC.)

Tartrate of Ammonia forms very soluble prismatic crystals, of a cooling taste. The addition of tartaric acid to its aqueous solution, produces a precipitate of a difficultly soluble *bitartrate* of ammonia.

Tartrate of Potassa is formed by saturating the excess of acid in *tartar*, by potassa. According to Mr. Richard Phillips, (*Remarks on the Pharmacopœia*,) 100 parts of tartar require 43.5 of carbonate of potassa. The resulting salt is soluble in less than twice its weight of water; it crystallizes in four-sided prisms, and consists of

1 proportional of acid	=	66
1 " potassa	=	48
		<hr/>
Tartrate of potassa	=	114

* Dr. Prout found tartaric acid, in crystals, composed of

Carbon	32
Water	36
Oxygen	32
	<hr/>
	100

Phil. Trans., 1827.
2 K 2

This salt is used in pharmacy as an aperient; it is the *potassæ tartas* of the *Pharmacopæia*. Its taste is saline, and somewhat bitter.

Bitartrate, or *Supertartrate of potassa*. *Tartar*.—This substance exists in considerable abundance in the juice of the grape, and is deposited in wine casks in the form of a crystallized incrustation, called *argol*, or *crude tartar*. It is purified by solution and crystallization, which renders it perfectly white: when in fine powder, it is termed *cream of tartar*.

The purification of tartar at Montpellier is performed as follows:—It is first dissolved in boiling water, and crystallized; these crystals are then boiled with one-twentieth their weight of pipe-clay, which absorbs the colouring matter, and falls as an insoluble sediment, the crystals of pure tartar separating afterwards upon the surface of the liquor, and upon the sides and bottom of the boiler; the term *cream of tartar* was originally applied to the imperfectly crystallized superficial crust. The details of this process are described by M. Fizes in the *Mémoires de l'Académie* for 1725; and it is still carried on upon the same plan.

The Venetian process for the purification of tartar consists in the separation of the grosser impurities by one or two preliminary solutions and crystallizations, after which, white of egg and wood-ash are added to the boiling solution of the crystals, and the impurities skimmed off during the effervescence which ensues.—DESMARET, *Journ. de Phys.* i. 67.

Bitartrate of potassa may be formed artificially by adding excess of tartaric acid to a solution of potassa. The mixture presently deposits crystalline grains, and furnishes a striking example of the diminution of solubility by increase of acid in the salt. Upon this circumstance, the use of tartaric acid as a test for potassa depends, for soda forms an easily soluble supertartrate, and consequently affords no precipitate.

Bitartrate of potassa is composed of

2 proportionals of acid	.	.	.	= 132
1 proportional of potassa	.	.	.	= 48
Bitartrate of potassa	.	.	.	<hr/> = 180

The crystals, the form of which has been described by Dr.

Wollaston, (THOMSON'S *Annals*, x. 37,) include one proportional of water, which is not separable at a heat much below that at which the acid of the salt begins to be decomposed. Their equivalent is, therefore, $180 + 9 = 189$.

The specific gravity of this salt is 1.95. It requires 120 parts of water at 60° , and 30 parts at 212° for its solution. It is rendered much more soluble by the addition of boracic acid or of borax, as was first observed by Le Fevre. (*Mém. Paris*, 1732.) Two parts of borax, and five of crystals of tartar in powder, are soluble in about six times their weight of boiling water; on evaporating the solution to the consistency of honey, the residue concretes into *Le Fevre's soluble cream of tartar*, or *sal gummosum*. It is the *tartarus boraxatus* of some old writers.

When exposed to heat, tartar fuses, blackens, and is decomposed, and carbonate of potassa is the remaining result. Provided the tartar be free from lime, which however is seldom the case, this furnishes a good process for obtaining pure carbonate of potassa. By destructive distillation, Fourcroy and Vauquelin obtained the following residuary substances from 1000 grains of crystals of tartar.—*Ann. de Chim.* lxiv. 43.

Carbonate of potassa	350
Carbonate of lime	6
Silica	1.2
Alumina	0.25
Iron and manganese	0.75

The aqueous solution of tartar becomes mouldy when exposed to air, and the tartaric acid being entirely decomposed leaves a weak solution of carbonate of potassa. Tartar sometimes acts as a simple acid, and dissolves oxides insoluble in most other acids; hence Gay-Lussac has suggested its use in certain analyses.—*Ann. de Chim. et Phys.* iii. 281. By the action of excess of caustic potassa, at high temperatures, tartar is converted into oxalate of potassa.

The component parts of tartar render it an excellent flux in the reduction of metallic ores upon a small scale, its alkali promoting their fusion, and the carbonaceous matter tending to reduce the oxides.

Tartar is sometimes adulterated by the addition of pounded quartz, and by calcareous spar; the former may be detected as an insoluble residue by boiling the powdered tartar with half its weight of carbonate of potassa or of borax in 8 parts

of water; the latter produces effervescence with dilute muriatic acid. A small portion of tartrate of lime is almost always present in the purified tartar; it separates in tufts of acicular crystals from the hot solution of the tartar.

Tartrate of Potassa and Ammonia is formed by saturating the excess of acid in tartar with ammonia. It effloresces and loses ammonia by exposure to air.

Tartrate of Soda forms acicular crystals soluble in their own weight of water. Tartaric acid, added to their solution, forms a *bitartrate of soda*, much more soluble than the corresponding salt of potassa. Tartrate of soda consists of 66 acid + 32 soda.

Tartrate of Potassa and Soda is prepared by saturating the excess of acid in tartar, with carbonate of soda; it is the *soda tartarizata* of the *Pharmacopæia*; it forms prismatic crystals, the forms of which have been described by Mr. Brooke. (*Ann. of Phil. N. S.* v. 451.) It has long been used in pharmacy under the name of *Rochelle Salt* and *Sel de Seignette*. According to Vauquelin's analysis (*FOURCROY'S Connaissances*, vii. 240), this salt consists of 54 tartrate of potassa + 46 tartrate of soda *per cent.*: these numbers agree with

2	proportionals of acid	.	.	.	= 132
1	„ potassa	.	.	.	= 48
1	„ soda	.	.	.	= 32
					<hr/>
					212

Dr. Thomson says that the crystals contain 8 proportionals of water.

Tartrate of Lithia is easily soluble; when its solution is evaporated it affords a white uncrystallized mass, opaque and not deliquescent. Excess of tartaric acid does not appear to give a bitartrate. It consists of 66 acid + 18 lithia = 84.

Tartrate of Potassa and Lithia, formed by saturating tartar with carbonate of lithia, affords quadrangular prismatic crystals, easily soluble and very slightly efflorescent.

Tartrate of Soda and Lithia forms rectangular four-sided prisms, easily soluble, slightly efflorescent, and of a pure saline flavour.

Tartrate of Lime is nearly insoluble in cold water, but soluble in 600 parts of boiling water; it is produced by adding chalk to tartar, as in the process for obtaining tartaric acid,

where it is decomposed by sulphuric acid. When dry it consists of 66 acid + 28 lime, and its equivalent is 94. Dried at a gentle heat it consists, according to Berzelius, of

1	proportional of anhydrous tartrate	.	= 94
4	„ „ water (9×4)		= 36
			<hr/> 130

Tartrate of Potassa and Lime may be formed by adding lime-water to solution of supertartrate of potassa, till it begins to become turbid: in a few days acicular crystals of the above triple salt are deposited, which effloresce when exposed to air.

Tartrate of Baryta is a difficultly soluble salt, composed of 66 acid + 78 baryta = 144. When carefully dried it is anhydrous: it is distinguished from sulphate of baryta by its solubility in muriatic, nitric, and acetic acids.

Bitartrate of Baryta forms transparent crystals, consisting of two proportionals of tartaric acid (66×2) = 132, one of baryta = 78, and two of water (9×2) = 18.

Tartrate of Strontia is thrown down on mixing the solutions of tartrate of potassa and nitrate of strontia. It dissolves in rather more than 300 parts of boiling water, and forms small rhomboidal crystals as the solution cools. Its equivalent is 118.

Tartrate of Magnesia is precipitated from the sulphate by tartaric acid: it is soluble in excess of tartaric acid, and forms a crystallizable salt. When dried at 60° , it consists of one proportional of anhydrous tartrate, and two of water. There is also a *bitartrate of magnesia*.

Tartrate of Manganese, formed by dissolving protoxide of manganese in tartaric acid, is a soluble salt, and therefore not precipitated by adding tartaric acid, or a neutral tartrate, to protomuriate or protosulphate of manganese.

When tartaric acid and black oxide of manganese are boiled together in water, carbonic acid is evolved, and a colourless solution of prototartrate of manganese is obtained. Formic acid is also produced during the action of the acid and oxide. —(*Quarterly Journal*, xiv. 232.)

Tartrates of Iron.—These salts have been little examined. Tartaric acid acts upon soft iron with the disengagement of hydrogen gas, and a difficultly soluble *prototartrate* of iron, nearly white and pulverulent, is formed. At a dull red heat,

this tartrate readily takes fire, and burns slowly away like tinder, the iron becoming peroxidized. It will probably form a valuable addition to the *Materia Medica*.—(URE, *Quarterly Journal*, Oct. Dec. 1829.)

Tartaric acid has scarcely any action upon the red oxide of iron, but a *pertartrate of iron* may be obtained by mixing the liquid red sulphate of iron with tartrate of potassa, in equivalent proportions. Sulphate of potassa precipitates in a crystalline powder, (the solutions being sufficiently concentrated,) which may be separated from the blood-red liquid pertartrate of iron by filtration. Alcohol forms a treacly precipitate in this solution.

Tartrate of Iron and Potassa.—This is the *Ferrum tartarizatum* of the *Pharmacopœia*: but it is most conveniently employed as a medicine in solution, which may be formed by digesting 1 part of soft iron filings with 4 of tartar; this mixture should be made into a thin paste with water, and digested for some weeks, till the acid is neutralized, fresh portions water being occasionally added to prevent exsiccation. The solution of this compound, which contains the iron in the state of peroxide, is possessed of some curious properties, first pointed out by Mr. R. Phillips.—*Experimental Examination of the London Pharmacopœia*, 98.

Tartrate of Zinc is formed by adding tartrate of potassa to sulphate of zinc, and appears to be a very difficultly soluble compound. Its theoretical composition is

$$\begin{array}{rcl} 1 \text{ proportional tartaric acid} & . & . & = 66 \\ 1 \text{ „ oxide of zinc} & . & . & = 42 \end{array} \Bigg\} 108$$

Tartrate of Tin.—Tartrate of potassa occasions a white precipitate in the protomuriate and permuriate of tin.

Tartrate of Potassa and Tin is formed by boiling the oxide in solution of tartar; it is very soluble, and the addition of alkalis and their carbonates occasion no precipitates.—THE-NARD, *Ann. de Chim.* xxxviii.

Tartrate of Copper is produced by adding tartaric acid to sulphate of copper. It forms a bluish-green crystallized precipitate.

Tartrate of Potassa and Copper is formed by boiling oxide of copper and tartar in water; the solution yields blue crystals

on evaporation; or if boiled to dryness, furnishes one of the pigments called *Brunswick green*.

Tartrate of Lead is thrown down in the form of an insoluble white powder, on adding tartaric acid to solution of nitrate of lead. It consists, according to Berzelius, of

Tartaric acid	.	.	.	37.5	=	66
Protoxide of lead	.	.	.	62.5	=	112
				<hr/> 100		<hr/> 178

When this tartrate is heated to a dull red in a glass tube, it acquires a brown colour; and, when cool, forms, as was first remarked by Dr. Gobel, a very perfect *pyrophorus*, which immediately inflames on being shaken out into the air. This property appears to depend upon the rapid oxidizement of the minutely divided metallic lead; or, perhaps, a very oxidizable carburet of lead may be formed. The charcoal is possessed of no peculiarities.

Tartrate of Potassa and Lead is formed, according to Thenard, by boiling a mixture of tartar and oxide of lead in water.—*Ann. de Chim.* xxxviii.

Tartrate of Antimony has not been examined.

Tartrate of Antimony and Potassa. Emetic Tartar.—This compound may be obtained by boiling protoxide of antimony, obtained by any of the processes formerly described, with pure supertartrate of potassa. It is the *antimonium tartarizatum* of the *London Pharmacopæia*.

Emetic tartar is usually prepared by boiling a solution of 100 parts of tartar with 100 parts of *finely levigated* glass of antimony, or of the protoxide described above (p. 84); the ebullition should be continued for half an hour, and the filtered liquor evaporated to about half its bulk, and set aside to crystallize: octoëdral and tetraëdral crystals of the emetic salt are thus obtained; and there is generally formed along with them a portion of tartrate of lime and potassa, which is deposited in small tufts of a radiated texture, and which may easily be separated when the mass is dried.

Mr. Phillips, in his *Experimental Examination of the London Pharmacopæia*, has stated several facts respecting the formation of this salt, which will be found useful to the manufacturer.

Emetic tartar is a white salt, slightly efflorescent, soluble in about 14 parts of cold and 2 parts of boiling water. It is decomposed by the alkalis; and when heated with ammonia, a portion of protoxide of antimony is thrown down, and a very soluble compound remains in the liquor. Sulphuretted hydrogen and hydrosulphuret of ammonia produce orange-coloured precipitates in its solution. It is decomposed by bitter and astringent vegetable infusions, but they do not render it inactive as a medicine. The most correct analysis of this salt appears to be that published by Mr. R. Phillips, which demonstrates it to consist, when in the form of crystals, of

1	proportional of bitartrate of potassa	.	=	180
3	„ protoxide of antimony	(52 × 3)	=	156
3	„ water	(9 × 3)	=	27
				<hr/> 363

Tartrate of Bismuth has not been examined, but moist oxide of bismuth, boiled with tartar, forms a difficultly soluble triple salt.

Tartrate of Cobalt.—Tartrate of potassa forms no precipitate in solutions of cobalt, but their colour is much heightened by it. Moist oxide of cobalt is soluble in tartaric acid, and the solution furnishes red crystals on evaporation.

Tartrate of Uranium is a very soluble salt, not easily crystallizable.

Tartrate of Titanium appears to be a soluble compound.

Tartrate of Cerium, according to Heisinger and Berzelius, is formed by adding tartrate of potassa to sulphate, nitrate, or muriate of cerium. It is a soft, tasteless powder, soluble in nitric, muriatic, and sulphuric acids, and in the alkalis.

Tartrate of Nickel, formed by digesting moist oxide of nickel in tartaric acid, is a very soluble salt; tartaric acid occasions no precipitate in the soluble salts of nickel.

Tartrate of Mercury.—Tartaric acid occasions white precipitates in all the solutions of the oxides of mercury not containing excess of acid.

Tartrate of Potassa and Mercury is formed, according to Thenard, by adding solution of tartar to protonitrate of mercury; and an analogous salt of the peroxide may be obtained by boiling it in a solution of tartar.

Tartrate of Silver.—Tartaric acid occasions no change in nitrate of silver, but tartrate of potassa forms a white precipitate, which is probably a tartrate of silver.

Tartrate of Silver and Potassa is thrown down by adding tartar to nitrate of silver.

Tartrate of Alumina is a soluble uncrystallizable compound of an astringent flavour.

ii. OXALIC ACID.

This acid is found in some fruits, and in considerable quantity in the juice of the *Oxalis Acetosella*, or *wood-sorrel*, and in the varieties of *rhubarb*. It is most readily procured by the action of nitric acid upon sugar, and has hence been termed *acid of sugar*.

It may be obtained by introducing into a retort 4 ounces of nitric acid diluted with 2 of water and 1 ounce of white sugar; nitric oxide gas is copiously evolved, and when the sugar has dissolved, about one-third of the acid may be distilled over: the contents of the retort are then emptied into a shallow vessel, and in the course of two or three days an abundant crop of white crystals is deposited, and, upon further evaporation of the mother-liquor, a second portion is obtained. The whole crystalline produce is to be redissolved in water, and again crystallized, by which the pure acid is obtained. In this way sugar yields rather more than half its weight of oxalic acid.

Oxalic acid thus procured is in the form of four-sided prisms, transparent, and of a very acid taste; the primary form of oxalic acid is a right rhombic prism, the modifications of which have been described by Mr. Brooke. The crystals dissolve in two parts of water at 60°, the specific gravity of the solution being 1.0593, and in their own weight at 212°; they also dissolve in boiling alcohol. When carefully dried, they fall to powder, and lose about one-third of their weight. They are composed, according to Berzelius (*Annales de Chimie*, lxxxi.), of

Real acid	52
Water	48
						<hr/> 100

Or of

1	proportional of acid	.	.	=	36
3	„ water	.	(9 × 3)	=	27
					<hr/>
	Equivalent of crystallized oxalic acid	.		=	63

Any attempt to expel the whole of the water by heat is attended by the decomposition of the acid.

When oxalic acid is submitted to the action of dry chlorine, the gas is slowly absorbed, and a white compound results, which is resolved by water into muriatic and carbonic acids. (*Ann. de Chim. et Phys.*, xix. 84.) By repeated distillation with nitric acid, oxalic acid is resolved into carbonic acid and water; and the acid itself, and the salts containing it, as is the case with the other vegetable acids, are decomposed by heat. By distilling oxalate of lime, Dr. Thomson found the acid resolved into five new substances; namely, water, carbonic acid, carbonic oxide, carburetted hydrogen, and charcoal.

Dobereiner was the first who suggested the non-existence of hydrogen in dry oxalic acid; and, according to Dr. Ure, (*Phil. Trans.* 1822, 480,) its ultimate constituents are,—

Carbon	.	33.34	= 2 proportionals	.	12
Oxygen	.	66.66	= 3 „	.	24
		<hr/>			<hr/>
		100			36

or we may represent it as composed of

1	proportional carbonic oxide	.	.	14
1	„ carbonic acid	.	.	22
				<hr/>
				36

This singular constitution of the anhydrous oxalic acid has already been adverted to under the compounds of carbon and oxygen. (Vol. i., p. 313.)

Speaking of the ultimate constitution of the crystallized oxalic acid, Dr. Prout observes, “many years ago I ascertained that this acid, in the crystallized state, consists of

Carbon	19.04
Water	42.85
Oxygen	38.11

a composition assigned to it long since by other chemists, and now I believe generally admitted, except by Dr. THOMSON, who informs us that he has met with a specimen containing as much as half its weight of water. I have examined a great many specimens with the view of verifying this result, but hitherto have not been successful.”

The number representing the oxalic acid, founded upon Dr. Wollaston's analysis of the binoxalate of potassa (*Phil. Trans.*, 1804), and upon Berzelius's analysis of the oxalate of lead (*Annales de Chimie*, No. 243), is about 36. According to the latter chemist, oxalate of lead consists of 24.54 oxalic acid + 75.46 oxide of lead.

The number deduced from the mean of the best analyses of oxalate of lime, is also 36; that number, therefore, may be adopted as the equivalent of oxalic acid, and the composition of the oxalates will be obvious accordingly.

Oxalate of Ammonia is a very useful test for the presence of lime. It crystallizes in long prisms, of which 45 parts require 1000 of water for their solution. Added to any soluble compound of lime, this salt produces an insoluble *oxalate of lime*, provided no excess of acid be present. Oxalate of ammonia consists of oxalic acid 36 + ammonia 17, its equivalent being 53; and its crystals include two proportionals of water. There is also a *binoxalate of ammonia*, less soluble than the oxalate, which consists of two proportionals of acid, one of ammonia, and eight of water.

Oxalate of Potassa forms flat rhomboidal crystals, soluble in rather less than 3 parts of water at 60°. It consists of 36 acid + 48 potassa, and the crystals include one proportional of water. The greater number of vegetable substances, such as cotton, wood, sugar, starch, gum, and most of the acids, and some animal substances, are converted into oxalic acid when fused with from four to six times their weight of caustic potassa, at a temperature below that which occasions charring: in this way oxalate of potassa is produced, and is converted, at a higher temperature, into carbonate of potassa.

Oxalate of potassa, dissolved in oxalic acid, produces the *bin-oxalate of potassa*, which crystallizes in small rhombic crystals, of a bitterish and sour taste, soluble in about 10 parts of cold water, and composed of

2	proportionals of	oxalic acid	.	.	=	72
1	„	potassa	.	.	=	48
2	„	water	.	.	=	18
						<hr/>
						138

This salt exists ready formed in the juices of the *oxalis aceto-*

sella, and is occasionally met with under the name of *salt of wood-sorrel*.

When binoxalate of potassa is digested in nitric or muriatic acid, half the potassa is abstracted and a compound remains, which has been called *quadroxalate of potassa*, consisting of

$$\begin{array}{rcl}
 4 \text{ proportionals of oxalic acid} & . & = 144 \\
 1 \quad \quad \quad \text{,,} \quad \quad \quad \text{potassa} & . & = 48 \\
 & & \hline
 & & 192
 \end{array}$$

The crystals of this salt include seven proportionals of water.

Oxalate of Soda is sparingly soluble in water, and separates from its solution in small crystalline grains, composed of 36 acid + 32 soda = 68. There is also a *binoxalate*, but no quadroxalate of soda.

Oxalate of Lithia is difficultly crystallizable and very soluble. The *binoxalate* forms small transparent granular crystals, not so soluble as the neutral salt.

Oxalate of Lime.—This compound is formed by adding oxalic acid or oxalate of ammonia to any solution of lime. It is insoluble in water, and in excess of oxalic acid, but dissolves in muriatic and nitric acids: hence in testing *acid solutions* for lime by oxalic acid, or oxalate of ammonia, the excess of acid should be previously neutralized. Dried at 100°, oxalate of lime retains two proportionals of water, and consists, therefore, of

$$\begin{array}{r}
 64 \text{ oxalate of lime} \\
 18 \text{ water} \\
 \hline
 82
 \end{array}$$

hence 82 of the precipitated oxalate thus dried, are only equivalent to 28 of lime, a circumstance which has sometimes been overlooked in analytical inferences. Whilst drying upon the sand heat this salt becomes singularly electrical. The anhydrous oxalate consists of 36 acid + 28 lime = 64 oxalate of lime.

The *Oxalates of Baryta and Strontia* are very nearly insoluble. They consist respectively of one proportional of each of their components. With excess of acid, baryta forms a soluble binoxalate, which shoots into acicular crystals, decomposable by mere solution in water. There appears to be no corresponding binoxalate of strontia.

Oxalate of Magnesia is a white, tasteless, and nearly insolu-

ble powder; yet it is not thrown down when oxalic acid, or even oxalate of ammonia, is added to sulphate of magnesia, unless the solutions are concentrated and hot. Hence oxalate of ammonia may be used to detect lime in solutions containing magnesia.

Oxalate of Manganese.—When black oxide of manganese and superoxalate of potassa are triturated together and moistened, carbonic acid is evolved; and, on adding more water, and filtering, a red solution, containing oxalic acid, potassa, and manganic acid is obtained, which after a time becomes colourless, and a triple salt is formed, containing the protoxide of manganese. Oxalic acid throws down a white powder from solutions of the protosalts of manganese.

Oxalate of Iron.—The *protoxalate* crystallizes in green prisms, and may be formed either by digesting the metal, or dissolving the protoxide in the acid. The *peroxalate* is thrown down from the permuriate or persulphate of iron, in the form of a difficultly soluble yellow powder, which is taken up again by excess of oxalic acid: hence the use of this acid in removing iron-moulds, which it does without injuring the texture of linen.

Oxalate of Zinc is formed by adding oxalic acid to a soluble salt of zinc: it is a white powder, nearly insoluble.

Oxalate of Tin is formed, according to Bergman, by digesting the metal in the acid: the solution, slowly evaporated, gives prismatic crystals.

Oxalate of Cadmium is a white insoluble powder.

Oxalate of Copper.—Oxalic acid oxidizes and dissolves copper. When oxalic acid is added to persulphate or pernitrate of copper, a difficultly soluble *peroxalate of copper* is thrown down. The theoretical composition of this salt is 1 proportional peroxide of copper = 80 + 2 of oxalic acid 72 = 152.

Oxalate of Copper and Ammonia.—This, and several other triple oxalates of copper, have been described by Vogel. (SCHWEIGGER'S *Journal*, vii.) By digesting peroxalate of copper in a solution of oxalate of ammonia, and filtering, rhomboidal crystals were obtained on evaporation, which detonated when suddenly heated: when slowly heated, they merely lost water and ammonia. From the analysis of this salt, it evi-

dently consists of 2 proportionals of oxalate of ammonia, 1 peroxalate of copper, and 6 water.

By digesting oxalate of copper in caustic ammonia, and pouring the solution thus obtained into a shallow basin, it deposits flat six-sided prisms of a blue colour, which effloresce on exposure to air. The undissolved portion of the oxalate also combines with ammonia, and produces another distinct compound. Dr. Thomson has given the following view of the composition of these salts.—*System*, ii. 624.

	1st Subspecies.	2d Subspecies.	3d Subspecies.
Oxalic acid	4 proportionals	2	2
Ammonia	2	2	1
Peroxide of copper	1	1	1
Water	6	2	0

Oxalate of Copper and Potassa is obtained by digesting percarbonate of copper in solution of binoxalate of potassa. Prismatic and rhomboidal crystals are formed, which Vogel considers as two distinct salts; the former, consisting of one proportional of oxalate of copper, two of oxalate of potassa, and *eight* of water; and the latter, of one proportional of oxalate of copper, two of oxalate of potassa, and *two* of water.

Oxalate of Copper and Soda.—Vogel has also described two subspecies of this salt.—SCHWEIGGER's *Journal*, vii.

Oxalate of Lead is thrown down in crystalline grains on adding oxalic acid to nitrate of lead. It is nearly insoluble in water, provided no excess of acid be present. It consists of

1 proportional of oxalic acid	.	.	= 36
1 „ oxide of lead	.	.	= 112
			<hr/> 148

When heated in a tube with potassium, it detonates violently.

Oxalate of Antimony has not been examined.

Oxalate of Bismuth is deposited in crystalline grains, when solution of oxalic acid is dropped into nitrate of bismuth.

Oxalate of Cobalt is an insoluble red powder, precipitated by oxalic acid from solutions of cobalt. It dissolves in excess of oxalic acid, and the solution furnishes crystals.

Oxalate of Uranium is a soluble compound.

Oxalate of Cerium is precipitated by the addition of oxalic acid or oxalate of ammonia to solutions of the protoxide of

cerium, of a white colour, insoluble in excess of acid, but soluble in liquid ammonia. In solutions of the peroxide of cerium, the precipitate is of a dingy red.

Oxalate of Nickel is thrown down from the nitrate in the form of an insoluble green powder.

Oxalate of Mercury is precipitated from the nitrates by oxalic acid. It is scarcely soluble, and detonates slightly when heated. It was supposed to exist in Howard's fulminating mercury, but this appears not to be the case.

Oxalate of Silver is an insoluble white powder, which blackens when exposed to light. It is precipitated on adding oxalic acid to nitrate of silver, and is soluble in nitric acid.

Oxalate of Alumina is easily formed by dissolving the newly precipitated earth in oxalic acid: it does not crystallize, but affords, on evaporation, a gelatinous mass, which deliquesces on exposure.

The oxalic acid, swallowed in large doses, is an active poison, and fatal cases are not unfrequent, in which this acid is taken, either intentionally or by mistake, for Epsom salt. The instant that the accident is discovered, a quantity of powdered chalk, diffused in warm water, should be taken, and vomiting excited as speedily as possible.

Many precautions have been recommended for the prevention of accidents of this kind: the only one requisite is to *taste* a grain or two of the crystals, when the pungent acid of the oxalic acid is easily and instantaneously distinguished from the bitter saline of the magnesian salt.

iii. CITRIC ACID.

Citric acid is obtained, by the following process, from lemon or lime juice:—

Boil the expressed juice for a few minutes, and when cold strain it through fine linen: then add powdered chalk as long as it produces effervescence; heat the mixture, and strain as before: a quantity of citrate of lime remains upon the strainer, which, having been washed with cold water, is to be

put into a mixture of sulphuric acid with 20 parts of water : the proportion of acid may be about equal to that of the chalk employed. In the course of 24 hours, the citrate of lime will have suffered decomposition, and sulphate of lime is formed, which is separated by filtration. The filtered liquor, by careful evaporation, as directed for tartaric acid, furnishes crystallized citric acid.

The preparation of this acid is carried on by a few manufacturers upon an extensive scale ; in different states of purity, it is employed by the calico-printers, and used for domestic consumption. Many circumstances which have not here been alluded to, are requisite to insure complete success in the operation ; these have been fully described by Mr. Parkes, in the third volume of his *Chemical Essays*. The average proportion of citric acid afforded by a gallon of good lemon juice, is about eight ounces. Dr. Henry states that he has obtained as much as twelve ounces.

Citric acid forms beautiful crystals, of which the primary form is a right rhombic prism. They have a very sour taste, and are soluble in somewhat less than their own weight of water at 60°. They contain, according to Berzelius, 100 real acid + 26.5 water, or

1	proportional of acid	.	.	.	=	58
2	„ water	.	.	.	=	18
						<hr/> 76

By exposure to heat a little below that which would decompose them, the crystals lose not more than 7 *per cent.* of water, so that the real quantity of water which they contain can only be learned from the analysis of a dry citrate. The analysis of this, as well as of the other vegetable acids given by Berzelius, differs considerably from that of Gay-Lussac and Thenard, in consequence, as it would appear, of the latter chemists having neglected the exclusion of water of crystallization. Berzelius gives its constituents as follow :—

Oxygen	.	.	.	54.831
Hydrogen	.	.	.	3.800
Carbon	.	.	.	41.369
				<hr/> 100

Dr. Prout finds the *crystals* of citric acid to consist of

Carbon	34.28
Water	42.85
Oxygen	22.87
						<hr/> 100

Dr. Ure's analysis nearly agrees with this, but the results are not such as to enable us to deduce from them the equivalent of the acid.

From the analysis of citrate of lead, the representative number of citric acid appears to be 58, a number which may also be obtained by supposing the dry acid to consist of

4 proportionals of oxygen	.	8×4	=	32
2 „ hydrogen	.	1×2	=	2
4 „ carbon	.	6×4	=	24
				<hr/> 58

Citric acid is sometimes fraudulently mixed with the tartaric: the adulteration may be discovered by gradually adding to the acid dissolved in water, a solution of carbonate of potassa, which will occasion the precipitation of bitartrate of potassa if tartaric acid be present.

When citric acid is distilled in a retort *per se*, an acid liquid is obtained, which, when saturated by lime, affords a precipitate, which may be decomposed by oxalic acid, and thus furnishes a peculiar product called, by Lassaigne, *pyrocitric acid*. It forms peculiar salts, perfectly distinct from the citrates, though its equivalent number is the same as that of citric acid. It consists of

Carbon	49.5
Oxygen	41.2
Hydrogen	9.3
					<hr/> 100

Citrate of Ammonia crystallizes with difficulty in prisms. 77 parts of the crystallized acid saturate 39 of common carbonate of ammonia.

Citrate of Potassa is very soluble, deliquescent, and difficultly crystallizable. It is much used in medicine as a mild diaphoretic, and is the *Salt of Riverius* of old pharmacy. The dry salt is composed of 58 acid + 48 potassa, and 76 parts of the crystallized acid saturate 70 of carbonate of potassa.

Citrate of Soda is difficultly crystallizable in hexaëdral tables, of a saline flavour, and soluble in somewhat less than two parts of cold water.

The equivalent of dry citrate of soda is 90, it being composed of 58 acid + 32 soda. 76 parts of the crystallized acid saturate 117 of crystallized carbonate of soda.

Citrate of Lithia is very difficultly soluble, and does not crystallize.

Citrate of Lime has been adverted to in the preparation of citric acid. It is nearly tasteless, and scarcely soluble in water, but readily soluble in solution of citric acid : when moistened, it soon grows mouldy if exposed to air. It consists of

1	proportional of acid	=	58
1	„	lime	.	.	.	=	28
							<hr/> 86

100 parts, therefore, of dry citrate of lime, may be regarded as composed of

Citric acid	67.6
Lime	32.4
							<hr/> 100

Citrate of Baryta is difficultly soluble, and forms acicular crystals, readily soluble in excess of nitric acid.

Citrate of Strontia is crystallizable and soluble.

Citrate of Magnesia does not crystallize.

Citrate of Manganese is formed by digesting moist protoxide of manganese in citric acid ; it produces white arborescent crystals.

Citrate of Iron.—According to Dr. Henry, (*Elements of Chemistry*, 9th Edit. ii. 200 ;) citric acid dissolves iron-filings with effervescence, and forms a nearly colourless solution, which deposits citrate of iron in the state of a white powder. It has a sweetish astringent taste ; dissolves in water, but not in alcohol ; and, when exposed in a moist state to the air, becomes first yellow, and then olive, being converted into a *per-citrate* which is uncrystallizable and deliquescent. There is also a *bicitrate* of the protoxide, which is deposited in a white crystalline form during the solution of iron in excess of citric acid ; it has a sour astringent taste, and is more permanent than the neutral protocitrate.

Citrate of Zinc.—Zinc dissolves in citric acid with effervescence: citric acid readily dissolves the oxide of zinc, and the solution deposits small crystals, scarcely soluble in water, and of an astringent taste.

Citrate of Tin.—Neutral citrate of potassa forms no precipitate either in protomuriate or permuriate of tin.

Citrate of Copper.—Citric acid forms a pale-blue precipitate in solution of sulphate and nitrate of copper.

Citrate of Lead is thrown down in the state of a nearly insoluble powder when citric acid is added to nitrate of lead. It consists of

58 acid
112 oxide
160

Citrate of Antimony is unknown.

Citrate of Bismuth is an insoluble white compound.

Citrate of Cobalt appears to be a soluble salt.

Citrate of Uranium—formed by digesting oxide of uranium in citric acid, is a soluble and difficultly crystallizable salt.

Citrate of Nickel is not thrown down by adding either citric acid or citrate of potassa to the solutions of nickel.

Citrate of Mercury.—Both the *protocitrate* and *percitrate* of mercury are insoluble, and thrown down when citric acid or a soluble citrate is added to the solutions of mercury.

Citrate of Silver is an insoluble white powder, which blackens when exposed to light.

iv. MALIC ACID.

The existence of a peculiar acid in the juice of apples was shown by Scheele, in 1785. He obtained it by adding solution of acetate of lead to the expressed juice of unripe apples, by which a *malate of lead* was formed, and afterwards decomposed by sulphuric acid. Vanquelin obtained it by a similar process, from the juice of the *houseleek*. The same acid exists, according to Braconnot, in the berries of the *mountain-ash*, from which it was first obtained by Mr. Donovan in 1815, and called by him *sorbic acid*; the apparent differences between the malic and sorbic acids are referable to the impuri-

ties of the former. Mr. Donovan has given the following process for its preparation. (*Phil. Trans.*, 1815.) Express the juice of the ripe berries, and add solution of acetate of lead, filter and wash the precipitate with cold water, then pour boiling water upon the filter, and allow it to pass through the precipitate into glass jars: after some hours crystals are deposited, which are to be boiled with 2.3 times their weight of sulphuric acid, specific gravity 1.090. The clear liquor is to be poured off, and, while still hot, a stream of sulphuretted hydrogen is to be passed through it, to precipitate the remaining lead; the liquid is then filtered, and when boiled so as to expel the sulphuretted hydrogen, is a solution of the pure vegetable acid.

M. Braconnot procures this acid by saturating the juice of the scarcely-ripe berries with chalk; during evaporation malate of lime falls, which he decomposes by carbonate of soda; the malate of soda is decomposed by acetate of lead, and treated by sulphuretted hydrogen as before described.

Malic acid may also be obtained by steeping sheet-lead in the juice of apples; in a few days, crystals of malate of lead form, which may be collected and decomposed by the very careful addition of dilute sulphuric acid.

When equal parts of sugar and nitric acid are distilled together till the mixture becomes brown, malic and oxalic acids are formed, but pure malic acid can scarcely be obtained by this process.

Malic acid, when carefully prepared, is a colourless liquid, very sour, and not susceptible of regular crystallization, though when very carefully evaporated it concretes into mammillary masses, showing traces of acicular crystals. Nitric acid converts it into oxalic acid. It forms crystallizable salts with many of the metallic oxides, which, however, have scarcely been examined with such precision as to enable us to determine the representative number of malic acid. With ammonia, potassa, and soda, it forms crystallizable salts, containing an excess of acid: added to acetate of lead, the precipitate is at first white and flocculent, but afterwards assumes a brilliant crystalline appearance. A detailed account of what is known respecting the malates will be found in M. Braconnot's Memoir. (*Annales de Chim. et Phys.*, tom. vi.)

When malic acid is submitted to destructive distillation, an acid sublimate forms in acicular crystals in the neck of the retort, and a sour liquor passes into the receiver, which, by evaporation, affords crystals of *pyromalic acid*. (LASSAIGNE, *Ann. de Chim. et Phys.*)

The ultimate component parts of this acid, according to Vauquelin, are

Hydrogen	16.8
Carbon	23.3
Oxygen	54.9
					<hr/>
					100

but, independent of other errors, the proportion of hydrogen is here greatly over-rated. It has more recently been analyzed by Dr. Prout (*Phil. Trans.* 1827), not *per se*, but in combination with lead, with lime, and with copper, and was found, abstracting water not essential to its composition, to consist of

Carbon	40.68
Water	45.76
Oxygen	13.56
					<hr/>
					100

The number 60 may be, probably, assumed as the equivalent of this acid, without material error.

V. GALLIC ACID.

This acid derives its name from the *gall-nut*, whence it was first procured by Scheele. It may be obtained by the following process :—

Digest bruised galls in boiling water, with about one-sixth their weight of vellum-cuttings, for some hours ; then allow the mixture to cool, and filter it. Add to the filtered liquor a solution of acetate of lead, as long as it occasions any precipitate ; pour the whole upon a filter, wash the precipitate with warm water, and digest it in very dilute sulphuric acid ; filter, and having saturated the clear liquor with chalk, evaporate to dryness. Introduce the dry mass into a retort placed in a sand-bath, and upon the application of heat a portion of water will first rise, and afterwards a crystalline sublimate of gallic acid.

There are many other processes for obtaining this acid, among which the following deserve notice: Moisten bruised gall-nuts, and expose them for five weeks to a temperature of about 80° . A mouldy paste is formed, which is to be squeezed dry, and digested in boiling water; it then affords a solution of gallic acid, which may be whitened by animal charcoal, and which, on evaporation, yields gallic acid, crystallized in white needles.—(BRACONNOT, *Annales de Chim. et Phys.*, tom. ix. 181.)

M. Baruel prepares gallic acid by adding a solution of white of eggs to infusion of galls till it ceases to produce a precipitate; it is then filtered, evaporated to dryness, and alcohol digested upon the residue. The alcoholic solution affords crystallized gallic acid by evaporation. (*Annales de Chim. et Phys.* x. 325.)

Boil an ounce of powdered galls in 16 ounces of water down to 8, and strain; dissolve 2 ounces of alum in water, precipitate the alumina by carbonate of potassa, and, after edulcorating it, stir it into the decoction; the next day filter the mixture; wash the precipitate with warm water, till this will no longer blacken sulphate of iron; mix the washing with the filtered liquor, evaporate, and the gallic acid will be obtained in acicular crystals.—(FIEDLER, *Nicholson's Journal*, i. 236.)

Gallic acid, when pure, is in whitish crystals, the forms of which have been described by Mr. Brooke. (*Annals of Phil.*, N. S., vi. 119.) They have a sour taste, and exhale a peculiar smell when heated. It dissolves in about 12 parts of water at 60° , and in rather more than two parts at 212° *. It is also soluble in alcohol and in ether. When repeatedly sublimed, this acid is altered and in part decomposed. It consists, according to Berzelius (*Annals of Philosophy*, vol. v.), of

Hydrogen	5.00
Carbon	56.64
Oxygen	38.36
					<hr/>
					100

* The aqueous solubility of this acid is very variously stated, and requires to be determined by new experiments.

And, according to the same authority, *gallate of lead* is composed of

Gallic acid	100
Oxide of lead	174

These proportions give the number 63 as the representative of gallic acid, and we may suppose it constituted of

3 proportionals of hydrogen	= 3	..	4.76
6 " carbon	= 36	..	57.14
3 " oxygen	= 24	..	38.10
	<hr/>		<hr/>
	63		100

The combinations of pure gallic acid with metallic bases have scarcely been examined, and consequently we have no accurate chemical history of the *gallates*. Their solutions are all very prone to decomposition, and the alkaline gallates acquire a deep brown colour, in consequence of the absorption of oxygen. This acid forms no precipitate in solutions of potassa or of soda, but when dropped into lime-water, baryta-water, or strontia-water, it occasions the separation of a difficultly soluble gallate of those earths. It also causes a precipitate in solutions of zirconia, glucina, and yttria. With the salts of iron, gallic acid produces a more or less intense violet-coloured discoloration, and ultimately a reddish-brown precipitate.

Gallic acid, when pure, affords no precipitate when added to solutions of animal jelly.

When an *infusion of galls* is added to certain metallic solutions, it forms precipitates composed of tannin, gallic acid, and the metallic oxide, and as these *tannogallates* are often of different colours, the infusion is employed as a test for such metals. The following metals in solution are thus thrown down, of the annexed colours:—

METAL.	SOLUTION.	PRECIPITATE.
MANGANESE .	Neutral protomuriate .	Dirty yellow
IRON . . .	Neutral protosulphate	Purple
Ditto . . .	Permuriate	Black
ZINC . . .	Muriate	Dirty yellow
TIN	Acid protomuriate .	Straw-colour
Ditto	Acid permuriate	Fawn-colour
CADMIUM .	Muriate	?
COPPER . .	Protomuriate	Yellow brown
Ditto	Pernitrate	Grass green
LEAD . . .	Nitrate	Dingy yellow
ANTIMONY .	Tartrate of antimony and potassa	Straw-colour
BISMUTH . .	Tartrate of bismuth and potassa	Yellow, and copious
COBALT . .	Muriate	0
URANIUM .	Sulphate	Bluish black
TITANIUM .	Acid muriate	Brown
Ditto	Neutral sulphate	Blood red
CERIUM . .		Yellowish
TELLURIUM .		Yellow
ARSENIC . .	White oxide	Little change
Ditto	Arsenic acid	0
MOLYBDENUM		Brown
NICKEL . . .	Sulphate	Green
MERCURY .	Acid protonitrate	Yellow
Ditto	Acid pernitrate	Yellow
Ditto	Corrosive sublimate	0
OSMIUM . .	Aqueous solution of oxide	Purple becoming blue
RHODIUM .		
PALLADIUM .		
SILVER . . .	Nitrate	Curdy and brown after some time
GOLD	Muriate	Deep brown
PLATINUM .	Muriate	Brownish green

The omitted metals are either not precipitated, or their action has not been examined.

Of these compounds, the *tannogallate of iron* is of the most importance, as forming the basis of writing ink, and of black dyes.

When an infusion of galls is dropped into a solution of sulphate of iron, it produces a deep purple precipitate, which is a very long time in subsiding; it becomes black by exposure to air. In writing ink, this precipitate is retained in suspension by mucilage, and the following proportions appear the best which can be used :

Finely-bruised galls, 3 ounces
Green vitriol (protosulphate of iron)
Logwood shavings
Gum arabic, of each 1 ounce
Vinegar, 1 pint.
Water, 1 ditto.

Put these ingredients into a bottle, and agitate them occasionally during twelve or fourteen days; then allow the coarser parts to settle, and pour off the ink for use. Sulphate and acetate of copper are not unfrequent ingredients in writing ink; they are supposed to give depth and permanence to its colour. M. Ribencourt gives the following recipe for good ink :—

Bruised galls	.	.	.	8 ounces.
Logwood chips	.	.	.	4 "
Sulphate of iron	.	.	.	4 "
Gum arabic	.	.	.	3 "
Sulphate of copper	.	.	.	1 "
Sugar-candy	.	.	.	1 "

Boil the galls and logwood in 12 pints of water down to 6; strain the decoction, and add the other ingredients, stirring the mixture till the whole is dissolved; then leave it to subside for twenty-four hours, and pour off the ink into bottles, which are to be well corked.

The tendency of ink to become mouldy is much diminished by keeping cloves in the ink-bottle, or by dissolving in each pint of the ink about three grains of corrosive sublimate.

The colour of common writing ink is apt to fade, in consequence of the decomposition of its vegetable matter: and when thus illegible, it may often be restored by washing the writing with vinegar, and subsequently with infusion of galls.

Acids also destroy its colouring matter, and those inks which resist their action, contain some other colouring principle; usually finely-powdered charcoal. Common writing ink is, for this reason, much improved by dissolving in the quantity above mentioned about an ounce of *Indian ink*, which is lamp-black, made into a cake with isinglass.

In dyeing black, the stuff is first impregnated with a solution of the gall-nut, and afterwards the colour is brought out by the application of sulphate, or acetate of iron.

Upon these subjects, much valuable information will be found in LEWIS'S *Philosophical Commerce of the Arts*, and in AIKIN'S *Dictionary*.

In the *Phil. Trans.* for 1817, I have described the properties of a species of galls from China, which furnish very pure gallic acid; and which, could they be abundantly obtained, would certainly prove a valuable substitute for common galls, in many of the processes in which they are employed.

vi. BENZOIC ACID.

Benzoic acid may be obtained by sublimation, from *benzoin*, which is a resinous exudation from the *Styrax benzoe* of Sumatra; it also exists in the *Balsams of Peru* and *Tolu*. If these substances be heated in a crucible, with a cone of paper attached to its mouth, the acid condenses in it in fine acicular crystals, which were formerly called *flowers of benzoin*. A good process for procuring this acid is that recommended by Mr. Hatchett, which consists in digesting benzoin in sulphuric acid, when it affords, on the application of heat, a copious sublimate of pure benzoic acid. (*Additional Experiments on Tannin, Phil. Trans.*, 1808.) It may also be obtained by boiling a pound and a half of powdered benzoin with 4 ounces of quicklime, in 6 or 8 quarts of water. When cold, the clear liquor is decanted, and the residuum again boiled in half the former quantity of water. The liquors thus obtained are boiled down to half their bulk, filtered, and mixed with muriatic acid, as long as it occasions a precipitate, from which the liquor is poured off, and when dry, it is put into an earthen vessel placed in a sand heat, and sublimed into paper cones*.

* Benzoic acid has also been found by M. Vogel in the Tonquin bean, and in the flowers of the *trifolium melilotus*; and by Mr. Accum in the pods of vanilla. It

In the tenth volume of Nicholson's *Journal*, I have detailed several experiments on benzoin, and have shown the relative quantity of acid afforded by the several processes which have been recommended for obtaining it, but different samples of benzoin afford very different relative proportions.

In making benzoic acid upon a large scale, the better kind of benzoin is most economically employed: it may be put into an iron pot, set in brickwork over a proper fire-place; the sublimate is most conveniently received into a large wooden box lined with paper, communicating by a conical iron or tin-plate neck with the subliming pot. The first product may be sublimed a second time in the same apparatus; and, by conducting the process rather rapidly, the acid condenses in beautiful prismatic crystals, somewhat elastic. If slowly sublimed, it is more powdery. By this process of sublimation, good benzoin yields 10 to 12 *per cent.* of acid contaminated by empyreumatic oil, and which, when pressed between folds of blotting paper, and again sublimed, is reduced to the proportion of 8 or 9 *per cent.* of the purified acid.

Benzoic acid, when it has been thus sublimed, is in the form of soft feathery crystals, very inflammable, fusible at about 230°, and of a specific gravity of about 67, of an acrid and slightly sour taste, soluble in 25 or 30 parts of boiling water, and very sparingly soluble in cold water. It is much more soluble in alcohol; and this solution easily furnishes it pure, and in prismatic crystals. It is soluble, without immediate change, in nitric and sulphuric acids, and in many other acids by the aid of heat. The oils also dissolve it.

Berzelius' analysis gives the following as the components of this acid:—

Hydrogen	5.16
Carbon	74.41
Oxygen	20.43
					<hr/>
					100

And benzoate of lead consists of

Benzoic acid	.	.	.	100
Oxide of lead	.	.	.	94
				<hr/>
				194

has also been found in urine, especially that of graminivorous quadrupeds. Some of the essential oils occasionally deposit benzoic acid.

Whence it appears that the representative number of benzoic acid is about 120.

To accommodate this result to the ultimate analysis, we may assume benzoic acid to include

6	proportionals of hydrogen	=	6	.	5
15	„ carbon	=	90	.	75
3	„ oxygen	=	24	.	20
			<hr/>		<hr/>
			120		100

According to Dr. Ure, the equivalent of benzoic acid is 116, constituted by

6	proportionals of hydrogen	=	6	.	5.16
13	„ carbon	=	78	.	67.24
4	„ oxygen	=	32	.	27.60
			<hr/>		<hr/>
			116		100

Dr. Henry very justly observes, in reference to these results, that the most accurate are probably those which indicate the greatest relative proportion of carbon, because it is more probable that too little carbonic acid should be found in the products of combustion, than too much; and, in the case of benzoic acid, its extreme volatility renders a portion likely to escape decomposition.

Benzoate of Ammonia forms deliquescent plumose crystals, very soluble in water. Berzelius recommends this salt as a precipitant of iron, which it throws down of an orange colour. According to Dr. Ure, 21.3 of ammonia take 15.7 of crystallized benzoic acid for saturation. Crystallized benzoate of ammonia consists, according to Thomson, of one proportional of acid, one of base, and one of water.

Benzoate of Potassa is a very soluble deliquescent salt; if it be digested with benzoic acid, a *bibenzoate of potassa* results, which, according to Bucholz, (*Ann. de Chim.*, lxxxiv.) forms acicular and lamellar crystals, requiring ten parts of water for their solution.

Benzoate of Soda forms efflorescent crystals, very soluble in water.

Benzoate of Lime forms acicular crystals, sparingly soluble in cold water. Vauquelin found this salt in the urine of the

cow. Benzoate of ammonia forms a copious white precipitate when added to muriate of lime, which is soluble in hot water.

Benzoate of Baryta is soluble and crystallizable.

Benzoate of Strontia is also a soluble salt.

Benzoate of Magnesia forms soluble plumose crystals.

Benzoate of Manganese forms beautiful prismatic crystals.

Benzoate of Iron.—Benzoate of ammonia forms an insoluble *perbenzoate* when added to solutions of peroxide of iron, of a yellow colour : in the protosalts of iron, it forms a white precipitate.

Benzoate of Zinc forms soluble acicular crystals when there is excess of acid : the neutral benzoate is insoluble.

Benzoate of Tin is insoluble.

Benzoate of Copper is a fine blue compound, difficultly soluble in water, but soluble in excess of benzoic acid.

Benzoate of Lead is insoluble, except there be excess of acid ; it then forms nacreous crystals.

Benzoate of Bismuth forms white acicular crystals, permanent in the air, soluble in water, and sparingly soluble in alcohol. (TROMMSDORF, *Ann. de Chim.*, xi.) When benzoate of ammonia is added to acid nitrate of bismuth, it forms an insoluble white precipitate ; Trommsdorf's salt therefore is probably a *bibenzoate*.

Benzoate of Cobalt.—Benzoate of ammonia forms no precipitate in solutions of cobalt.

Benzoate of Uranium is a difficultly soluble straw-coloured compound, when formed by adding benzoate of ammonia to nitrate of uranium.

Benzoate of Nickel.—Solutions of nickel are only rendered slightly turbid by benzoate of ammonia ; benzoate of nickel is probably therefore a soluble salt.

Benzoate of Mercury.—Benzoic acid forms white precipitates in the solutions of mercury.

Benzoate of Silver, obtained by digesting moist oxide of silver in benzoic acid, forms acicular crystals ; but benzoate of ammonia forms an abundant insoluble precipitate in solution of nitrate of silver.

Benzoate of Alumina forms arborescent crystals.

Besides the vegetable acids which have now been described, there are a few others of considerably inferior interest and importance; namely, the

Moroxylie Acid, discovered by Klaproth in the bark of the *morus alba*, or *white mulberry*. (NICHOLSON'S *Journal*, vii.) An exudation was observed upon this bark, which proved to be a compound of a peculiar acid and lime, or a *moroxylate of lime*; its solution was decomposed by acetate of lead, and the *moroxylate of lead* thus obtained, decomposed by dilute sulphuric acid, furnished a solution of moroxylie acid, which gave acicular crystals on evaporation. This acid has the taste of succinic acid; it is soluble in water and alcohol, and does not, like some of its salts, form precipitates in metallic solutions. The quantity of this acid examined by Klaproth was so small, as to leave some doubt respecting its distinct nature.

Boletic Acid was obtained by Braconnot from the *boletus pseudo-ignarius* (*Ann. de Chim.* tom. lxxx.) by cautiously evaporating its expressed juice to the thickness of syrup, digesting it in alcohol, dissolving the residue in water, and adding nitrate of lead to the aqueous solution; the precipitate washed and diffused through water, was decomposed by sulphuretted hydrogen; the liquor was then filtered and evaporated till it formed crystals, which were purified by solution in alcohol and evaporation. These crystals are boletic acid; they are prismatic, and require 180 parts of water at 68°, and 45 of alcohol for their solution, which reddens blues, and precipitates nitrate of lead, and the salts containing the peroxide, but not those of the protoxide of iron. This acid sublimes, with little alteration, when heated. Braconnot has examined the *boletates of ammonia, potassa, lime, and baryta*, but his researches have not as yet been confirmed by any other chemist.—THOMSON'S *Syst.* sixth edit. ii. 157.

Fungic Acid was procured by the same chemist from the *boletus juglandis*, and some other fungi; it is deliquescent and uncrystallizable.—*Ann. de Chim.*, lxxxvii.

In the astringent root of the *Krameria triandra*, M. Peschier has announced the existence of what he considers as a distinct substance, which he calls *krameric acid*.—*Journal de Pharmacie*, vi.

M. Braconnot has given the term *Ellagic acid* (from the

word *galle* reversed) to an acid body which he has detected, along with gallic acid, in infusion of galls, but its characters have been but imperfectly ascertained.

Zumic acid was discovered by the same chemist in vegetable substances, which have undergone acetous fermentation.—*Thomson's Syst.* Vol. ii. p. 189.

Formic Acid.—The peculiarities of an acid obtained by the distillation of *ants*, was first noticed by Fischer and Margraaf; but it was afterwards regarded as identical with acetic acid, upon the authority of Fourcroy and Vauquelin (*Ann. de Chim.* lxiv. 48). Gehlen, however, (*Thomson's Annals*, v. 24) and more lately Berzelius, have shown that it is a distinct compound; and Döbereiner has published some curious facts respecting its artificial production.—(*Quarterly Journal*, xiv. 233, *O. S.*) It may be obtained from a mixture of tartaric acid, black oxide of manganese, and water; or more abundantly from a mixture of 2 parts of crystallized tartaric acid, 5 of peroxide of manganese, 5 of sulphuric acid, and 5 of water. Soon after mixture, these ingredients, which should be in a sufficiently capacious vessel, effervesce violently, and give off abundance of carbonic acid; if afterwards distilled, the formic acid passes over: it possesses several peculiarities, which amply distinguish it from acetic acid, among which the most remarkable is in the action of sulphuric acid, which converts it into water and carbonic oxide; and if sulphuric acid be poured upon *formiate of potassa*, which is a deliquescent and difficultly crystallizable salt, of a saline bitter taste, an effervescence ensues, attended by the escape of *carbonic oxide* only. The formic acid is converted into carbonic acid by the nitrates of silver and of mercury, those salts being, at the same time, reduced to the metallic state.

The ultimate components of formic acid are, according to Berzelius,

Carbon	32.970
Oxygen	64.223
Hydrogen	2.807
					<hr/>
					100

If we submit these proportions to the theory of equivalents, we may regard formic acid as composed of

2	proportionals of carbon	(6 × 2)	=	12	.	32.4
3	„ oxygen	(8 × 3)	=	24	.	64.8
1	„ hydrogen	.	=	1	.	2.8
				<hr/>		<hr/>
				.37		100

The *Formiate of Lead*, which is a crystallizable salt, soluble in about 36 parts of cold water, consists, according to Berzelius and Lecanu, of 25.12 acid + 74.88 oxide; and these proportions would give nearly the same equivalent. It is remarked by Dr. Henry, in reference to these results, that, if worthy of confidence, they shew a material difference between the constitution of formic and acetic acids, the latter of which contains 4 proportionals of carbon + 3 of oxygen + 2 of hydrogen, and is represented by the equivalent 50. The acid, he observes, to which the formic most nearly approaches, is the *oxalic*, from which it differs only in containing an atom of hydrogen, in addition to the carbon and oxygen. It may be added, that many of the properties ascribed by Mr. Daniell to lamic acid, coincide with those of the formic.

Formiate of Ammonia forms plumose crystals, readily soluble in water. This salt volatilizes when heated. *Formiate of Soda* yields rhombic crystals, of a saline and bitter taste, which fuse when heated, and lose water of crystallization. Exposed to a red heat, this salt affords 0.366 pure soda. It consists, according to Göbel, 36.6 soda, 43.4 formic acid, and 20 water; or, probably, of 1 proportional of soda; 1 of acid, and 2 of water. *Formiate of Baryta* crystallizes in transparent prisms, of a bitter taste, and permanent in the air at common temperatures. When heated, it becomes brown, and exhales the smell of burned sugar. It is soluble in 4 parts of cold water, and insoluble in alcohol. It has been analyzed, with nearly corresponding results, by Richter, Gehlen, and Göbel; and may be regarded as a compound of 1 proportional of baryta = 78 + 1 of formic acid = 37. *Formiate of Strontia* is also a crystallizable salt. *Formiate of Lime* yields six-sided prismatic crystals, of a bitter and salt taste, which effloresce in the air, and decrepitate in the fire; they are soluble in 8 parts of water at 60°, and insoluble in alcohol. Deprived of water,

this salt consists, according to Richter, of 77.9 lime + 100 acid; numbers not much at variance with 1 proportional of lime = 28 + 1 proportional of formic acid = 37. *Formiate of Magnesia* crystallizes in small cubes, or acicular groups, soluble in 13 parts of water at 60°, and insoluble in alcohol. They are anhydrous, and contain one proportional of each component. *Formiate of Manganese* crystallizes in flat prisms, soluble in 15 parts of cold water, insoluble in alcohol, and containing one proportional of base, one of acid, and one of water. *Formiate of Iron*, with the protoxide, cannot be obtained in a solid form: with the peroxide, small brown acicular crystals are formed, very soluble in water, and difficultly in alcohol. *Formiate of Zinc* yields cubic crystals, difficultly soluble in water, and insoluble in alcohol. *Formiate of Cadmium* yields cubes and rhombs, of a sweetish metallic taste; they include two proportionals of water of crystallization. *Formiate of Tin* is not permanent. *Formiate of Copper* crystallizes in flat prisms, of a green-blue colour, efflorescent in warm air, and burning with a green flame: they dissolve in 8 parts of water at 60°, and are slightly soluble in alcohol: they consist, according to Göbel, of 35.83 peroxide of copper, 32.74 formic acid, 31.86 water; numbers which nearly accord with *one* proportional of peroxide, *two* of formic acid, and *four* of water*.

Section XIX. SALIFIABLE, OR ALKALINE BASES IN VEGETABLES.

THE discovery of these substances is one of the most curious and important of modern chemistry. The first of them was detected in opium in 1816, by Sertuerner of Einbeck, near Hanover. Several others were afterwards pointed out by Pelletier and Caventou, and among them cinchonia and quinia,

* The above abstract of the properties of the *formiates*, is chiefly from the authorities of Göbel, Süersen, and Döbereiner. I have placed the formic acid in the present chapter, on account of its obvious analogies to the vegetable acids.

which have proved of so much use in medicine; and more lately, some others of minor importance have been added to the list. These salifiable bases appear all to contain nitrogen as one of their ultimate elements; they have a bitter taste, are very sparingly soluble in water, more soluble in alcohol, and readily soluble in most of the dilute acids: with infusion of galls, they furnish difficultly soluble precipitates, and their compounds with the acids are decomposed and precipitated by the alkalies. They are mostly crystallizable, and are represented by very high equivalent numbers. They restore the blue colour to reddened litmus. They are found in plants united to certain acids, and usually forming neutral or acid salts.

Morphia may be obtained from powdered opium by triturating it into a paste with dilute acetic acid: pour caustic ammonia into the filtered solution, and evaporate; during the evaporation, a brownish substance separates, which, by digestion in a small quantity of cold alcohol, becomes nearly colourless, and is pure morphia. It may also be procured by boiling a concentrated infusion of one pound of opium with 150 grains of pure magnesia, for about a quarter of an hour; a grey deposit falls, which is to be washed, dried, and digested in warm dilute alcohol, by which a large portion of colouring matter is dissolved; the residue is then to be washed with a little cold alcohol, and boiled in a large quantity of alcohol, specific gravity 820. The liquid, if filtered while hot, deposits crystalline morphia on cooling. If coloured, it may be purified by two or three successive crystallizations from solution in strong alcohol.

Morphia is sparingly soluble in water, but readily soluble in alcohol and in ether, from which it may be obtained in prismatic and octoëdral crystals. Its primary form is a right rhombic prism. (BROOKE.) It requires 82 parts of boiling water, 36 of boiling alcohol, 42 of cold alcohol, and 8 of sulphuric ether for its solution. It is highly poisonous and narcotic, even when administered in very small doses; it is fusible, and crystallizes as it cools. It is easily combustible, and when heated in close vessels, leaves a black matter having a peculiar smell.

Morphia possesses the general characteristic properties of an alkali; it reddens turmeric, and forms neutral crystallizable compounds with the acids.

Muriate of Morphia forms plumose crystals, soluble in about ten parts of water at 60° , and composed of

35	Muriatic acid,
41	Morphia,
24	Water.
<hr/>	
100	

Nitrate of Morphia forms acicular crystals, soluble in 1.5 of water, at 60° , and composed of

20	Nitric acid,
36	Morphia,
38	Water.
<hr/>	
100	

Sulphate of Morphia crystallizes in prisms, soluble in two parts of water, at 60° , and composed, according to Pelletier and Caventou, (*Journal de Pharmacie*, v.) of

11	Sulphuric acid,
89	Morphia.
<hr/>	
100	

Phosphate of Morphia, when neutral, crystallizes in cubes.

Carbonate of Morphia forms prismatic crystals, soluble in four parts of water at 60° , and containing, according to Choulant, (*Ann. of Phil.* xiii.)

28	Carbonic acid,
22	Morphia,
50	Water.
<hr/>	
100	

The existence of this salt is however denied by Sertuerner.

Acetate of Morphia forms delicate acicular crystals. This salt has been lately much employed in medicine as a sedative: it appears to tranquillize the system more effectually than opium. The above salts have a bitter taste, and are decomposed by ammonia. Infusion of galls occasions a white cloud in a solution containing not more than a fifteen-thousandth part of morphia. Nitric acid forms a red solution with morphia, and ultimately converts it into oxalic acid.

Acetate of morphia has been occasionally resorted to for cri-

minal purposes; and, in consequence of its want of odour, it cannot be so easily detected as opium. Lassaigne recommends the following method for discovering its presence, (*Ann. de Chim. et Ph.* xxv. 102,) but it is not very effective. The suspected solution is evaporated in a water bath, and the residue digested with alcohol: the alcoholic solution is evaporated, and water added to its residue, which takes up the acetate, if present, and yields it in acicular crystals when left to spontaneous evaporation; it is known by its bitter taste—by yielding a precipitate with ammonia, and with infusion of galls—by disengaging acetic acid when moistened with sulphuric acid—and by the orange-red colour produced by nitric acid. It is said, that morphia, when pure, is so insoluble as scarcely to act as a poison, for Orfila gave twelve grains of it to a dog without effect; but, in the human stomach, the case may be very dissimilar; at all events, if it meet with acid in the stomach, the probability is, that it would be rendered soluble and intensely poisonous.

The ultimate components of morphia have been determined by Pelletier and Dumas (*Ann. de Chim. et Phys.* xxxiv.), by Bussey (*Ann. de Phil. N. S.* vi.), and by myself (*Quarterly Journal, O. S.* xvi.), with the following results:—

	Pelletier and Dumas.	Bussey.	Brande.
Carbon . . .	72.02 . . .	69.0 . . .	72.0
Oxygen . . .	14.84 . . .	20.0 . . .	17.0
Hydrogen . .	7.61 . . .	6.5 . . .	5.5
Nitrogen . .	5.53 . . .	4.5 . . .	5.5
	<hr/> 100	<hr/> 100	<hr/> 100

These experiments afford results too much at variance to furnish data upon which to calculate the equivalent of morphia: from the analysis of some of its saline combinations, it would appear that its representative number is about 325.

Meconic Acid.—In opium, morphia is said to be combined with a peculiar acid, which has been called the *meconic acid*, and this combination is decomposed by the action of ammonia or of magnesia in the preparation of morphia.

The following process is said to afford pure meconic acid: Boil infusion of opium with magnesia, and digest the precipitate in hot alcohol to remove morphia; *meconiate of magnesia*

remains: dissolve this in dilute sulphuric acid, and add muriate of baryta,—a precipitate falls, composed of sulphate and *meconiate of baryta*; digest this in dilute sulphuric acid, which decomposes the meconiate; filter and evaporate, till brown crystals of impure meconic acid are deposited; dry these crystals, and then heat them carefully in a retort to sublime the meconic acid. White crystals are thus obtained, which fuse at 250° , and sublime without decomposition; they are sour, and very soluble in water and alcohol.

Dr. Ure recommends acetate of lead, acidulated by acetic acid, as a preferable precipitant for meconic acid, the excess of acetic acid preventing the falling down of morphia. 100 grains of the best opium afford 27 grains of washed (but not quite pure) *meconiate of lead*: this, diffused in water and decomposed either by dilute sulphuric acid, or by a current of sulphuretted hydrogen, furnishes a solution which, when filtered and slowly evaporated, yields granular crystals of meconic acid.

The most distinctive character of meconic acid, applicable as a test of its presence, was originally pointed out by Vogel, namely, that it produces a peculiar red colour with the persalts of iron; hence the persulphate or permuriate of iron may be used as tests of its presence; and Dr. Ure, observing that the quantity of meconic acid in any given sample of opium, must be in equivalent ratio to that of the morphia, has ingeniously proposed to determine the relative values or narcotic powers of different opiums by the intensity of discolouration which their infusions suffer from permuriate of iron. “Let a grain or two of each be dissolved in a little dilute alcohol, and then diffused through such a body of water as will make the liquid nearly colourless. Pour each liquid into a graduated glass cylinder, and add to it a few drops of red muriate (or tincture of muriate) of iron, the characteristic brown-red tint will immediately appear of a depth proportional to the meconic acid, and equivalent to the morphia present, for the previous dilution with water has been so great as to remove the inequalities of colour in the original spirituous solutions. Let the darker shades be now lightened with water till the tints of the whole be uniform, and the relative colours of the liquids will afford an approximate measure of the qualities of the several opiums.”

In cases of judicial inquiries, it has been proposed to determine the presence of opium in the contents of the stomach by the red colour produced by a persalt of iron; but there are several reasons why the test cannot be depended upon, and among them the presence of sulphocyanate of potassa in the saliva, consequently, also, in the stomach; which sulphocyanate reddens the solutions of peroxide of iron in a manner so similar to meconic acid, as to invalidate the use of the test.

Meconiate of Ammonia forms stellated crystals, soluble in 1.5 parts of water, at 60°, and composed, according to Choulant, of

42 Ammonia,
40 Meconic acid,
18 Water.

100

Meconiate of Potassa forms four-sided tables, soluble in two parts of water at 60°, and composed of

60 Potassa,
27 Meconic acid,
13 Water.

100

Meconiate of Soda forms efflorescent prismatic crystals, soluble in five parts of water at 60°, and composed of

40 Soda,
32 Meconic acid,
28 Water.

100

Meconiate of Lime affords prismatic crystals, soluble in about eight parts of water at 60°, and consisting of

42 Lime,
34 Acid,
24 Water.

100

The equivalent number of meconic acid, deduced from the above analyses by Choulant, will be about 21.

Narcotine.—When an aqueous extract of opium is digested

in ether, the latter, upon spontaneous evaporation, deposits a crystallized substance, which was first described in 1803 by Derosne, and was regarded as a compound of morphia, until Robiquet proved that it was a peculiar principle, and gave it the above name. Although acids increase the solubility of narcotine, they do not combine with it into saline compounds, nor has narcotine any of the other properties of the vegetable alkaline bases. Narcotine is nearly insoluble in cold, and but little soluble in hot water. It dissolves in alcohol, ether, and oil; and, in the aqueous infusion of opium, appears to be dissolved by the aid of an acid, probably distinct from the meconic. Its ultimate constituents, according to Pelletier and Dumas, are

Carbon	68.88
Oxygen	18.00
Nitrogen	5.91
Hydrogen	7.21
						<hr/> 100

It resembles the vegeto-alkalis, therefore, in containing nitrogen. It is supposed, that the stimulating effects of opium depend upon the presence of narcotine, whilst its purely sedative qualities are referable to morphia. It must, however, be admitted, that the composition of the active principle in crude opium is yet imperfectly understood; and it is possible, that narcotine, in some peculiar state of combination, may contribute to its powerful qualities: it cannot be admitted that they are referable to morphia only, for a hundred parts of opium do not yield more than seven of that base; so that, were morphia the true active essence of the poppy, it should produce (when extracted in its active saline state of sulphate or acetate) effects commensurate in energy with the fourteen-fold concentration which the opium has undergone; yet morphia, or rather its soluble salts, may be given in nearly the same doses as crude opium; and a grain of opium and a grain of acetate of morphia are not widely different in their operation as sedatives. In reference to this interesting subject, Dr. Ure has remarked, (in a manuscript paper which he is about to publish, but which he has allowed me to quote here,) “that since opium affords to ether and to ammonia a fatty matter and a resin, it is pos-

sible that the union of an oleate or margarate of morphia with narcotine, may confer upon it peculiar activity, promoted perhaps by the presence of meconic acid."

Experiments upon the respective narcotic and other medical properties of the different combinations of morphia are still wanting; and the same remark applies to cinchonia and quinia. Hitherto, the acetates and sulphates are the only artificial compounds of those bases which have been much attended to; but when we reflect upon the important part which the acid performs in affecting the medical qualities of other bases, (how different, for instance, is the *nitrate* from the *sulphate* of potassa, &c.,) it is possible, that the different salts of morphia, &c., may be possessed of extremely different and even opposite virtues.

Strychnia.—MM. Pelletier and Caventou, in analyzing the bean of *St. Ignatius* (*Strychnos Ignatia*), and the *vomica nut* (*Strychnos nux vomica*), discovered in them a peculiar principle, which they have termed *Strychnine*, and which, like morphia, possesses alkaline properties. The following is their process for obtaining it:—Digest the raspings of the bean in sulphuric ether, which separates a green oily fluid; pour this off, and treat the residuum with alcohol; filter the latter solution when cold, and evaporate; it leaves a brown bitter substance, soluble in water and alcohol; to its strong aqueous solution add a solution of potassa, which causes a precipitate, which, when washed with a little cold water, is white, crystalline, and very bitter. If not quite pure, it may be rendered so by solution in acetic acid, and precipitation by potassa.

Strychnia is nearly insoluble in water; it dissolves in alcohol and ether, and the solutions are intensely bitter and poisonous. It re-produces the blue of vegetable colours reddened by acids. It crystallizes in small quadrangular prisms; it has no smell, and is neither fusible nor volatile, but is decomposed at about 600°.

According to Pelletier and Dumas, the ultimate components of strychnia are

Carbon	78.22
Nitrogen	8.92
Hydrogen	6.54
Oxygen	6.32

The poison of the upas tree, and the poisonous extract used by the American Indians to anoint the barbs of their arrows, called worara, afford a vegeto-alkaline base resembling strychnia.

The *Salts of Strychnia* are decomposed by potassa, soda, ammonia, baryta, strontia, and magnesia, the base being thrown down; most of the other metallic salts are decomposed by strychnia, and with some it forms triple salts.

Sulphate of Strychnia forms cubic crystals, soluble in about 10 parts of water at 60°; its taste is bitter, and it is decomposed by the alkalis. It consists of

Sulphuric acid	9.5
Strychnia	90.5
					<hr/> 100

Muriate of Strychnia crystallizes in acicular prisms, more soluble than the sulphate.

Nitrate of Strychnia is formed by digesting excess of strychnia in very dilute nitric acid; it yields stellated crystals, which acquire a red colour by the action of sulphuric acid. Nitric acid, poured upon strychnia or its salts, produces a deep red colour.

The discoverers of strychnia assert that it exists in the above-mentioned seeds, combined with a peculiar acid, somewhat resembling the malic, but susceptible of crystallization; they have called it *Igasuric Acid*, and the poisonous principle existing in the seeds, appears to be *igasurate of strychnia*.

Delphia is an alkaline principle, discovered by MM. Las-saigne and Feneulle in the seeds of stavesacre (*Delphinium Staphysagria*). They obtained it by the following process:—The seeds, deprived of their husks, were boiled in distilled water, the decoction filtered, boiled with a portion of pure magnesia, and re-filtered; the residue upon the filter was then boiled with highly rectified alcohol, by which the alkali was separated and obtained by evaporation, in the form of a white pulverulent substance.

Delphine, when pure, appears crystalline in its moist state; its taste is bitter and acrid; when heated, it melts, and on cooling becomes brittle like resin; it is sparingly soluble in

water, but readily soluble in alcohol and ether; it renders the blue of violets green, and forms very soluble salts with the acids, from which the alkalis precipitate delphine in a white gelatinous state.—*Ann. de Chim. et Phys.* xii. 358.

Veratria.—(*Ann. de Chim. et Phys.* iv. 69. *Quarterly Journal*, x. 171.) The seeds of the *veratrum sabadilla*, and the roots of the *veratrum album*, or white hellebore, contain a vegeto-alkaline base, united with gallic acid. It is most readily procured from the seeds of the *sabadilla*, which are first digested in ether, to remove oily matter, then boiled in alcohol, and the solution suffered to cool; it is then filtered, evaporated to dryness, and the residue digested in water; which, being partly evaporated, deposits a yellow matter, to be separated by filtration. The clear solution is now mixed with acetate of lead, which gives a precipitate, to be removed by filtering; and the filtered liquor (its lead having been separated by sulphuretted hydrogen, and heated) is now boiled with magnesia; the precipitate thus produced is digested in boiling alcohol, from which the *veratria* is deposited in a pulverulent form, on evaporation. If not at first white, it may be rendered so by a second solution, and by the aid of animal carbon.

Veratria is not crystallizable; it has a pungent, but not a bitter taste, and powerfully irritates the nostrils. A very small dose produces nausea and vomiting. It fuses at a temperature of 122° , and concretes, on cooling, into a translucent yellow mass. Boiling water does not take up more than a thousandth part of its weight, but it is readily soluble in alcohol, and less so in sulphuric ether. It consists, according to Pelletier and Dumas, of

Carbon	66.75
Nitrogen	5.04
Hydrogen	8.54
Oxygen	19.60
Loss	0.07
						<hr/> 100

Veratria has also been discovered in the roots of the *colchicum autumnale*, or meadow saffron; and it is probably the

principle to which the curative powers of that drug, in cases of gout, are referable.

It is curious that, many years ago, Mr. Moore suspected the active ingredient in the celebrated French gout specific, called *Eau Medicinale d'Husson*, and which is a vinous infusion of colchicum, to be derived from hellebore, which we now know to contain the same alkaline base as colchicum.

Brucia.—According to Pelletier and Caventou, this peculiar salifiable base is contained in the bark of the *brucia antidysenterica* *. The bark having been previously digested in sulphuric ether, is treated with alcohol, the alcoholic solution evaporated, and the residue dissolved in water, saturated with oxalic acid, and evaporated to dryness. Alcohol, digested upon this residuum, dissolves colouring matter, and leaves pure oxalate of brucia, which may be decomposed by lime, and the brucia dissolved out by boiling water, of which it requires about 500 parts for solution. Brucia forms anhydrous prismatic crystals, of an acrid, bitter taste, fusible a little above 212° , and concreting into a waxy mass. It consists, according to Pelletier and Dumas, of

Carbon	.	.	.	75.04
Nitrogen	.	.	.	7.22
Hydrogen	.	.	.	6.52
Oxygen	.	.	.	11.21
				<hr/> 100

Brucia appears to be combined, in the bark, with gallic acid. In the *nux vomica*, it is united with strychnia.

The salts of brucia are very bitter, and mostly crystallizable. They are poisonous, but apparently less so than the corresponding compounds of strychnia. It appears probable that brucia bears the same relation to strychnia that quinia does to cinchonia; and it is not improbable that quinia is an oxide of cinchonia.

Atropia was discovered by Brandes in the decoction of the leaves of the *atropa belladonna*. When potassa is

* This is sometimes referred to as the genuine *Angustura* bark (*cusparia febrifuga* of the Pharmacopœia), which does not contain the base in question. It is probably the bark known in this country under the name of *spurious Angustura*, and which has generally been considered as obtained from a species of *strychnos*.

dropped into a strong decoction of these leaves, the precipitate which falls contains the atropia, and much foreign matter, separable by redissolving the precipitate in a dilute acid, and again decomposing by lime or magnesia. Boiling alcohol separates the atropia from the last precipitate when dried, and yields, by the help of animal charcoal, white atropia on evaporation. Cold water and cold alcohol scarcely dissolve it, but boiling water takes it up in larger proportion, and boiling alcohol copiously dissolves it. With the acids it forms definite salts, the greater number of which are soluble, and very poisonous.

Hyoscyamia.—The same chemist has announced the presence of an alkaline base in the leaves of the *hyoscyamus niger*, forming prismatic crystals and definite salts. We have endeavoured to obtain this principle, but hitherto without success.

Digitalia has been stated to exist in the leaves of the *digitalis purpurea* by M. Royer. (*Quarterly Journal, O. S.*, xviii. 178.) He describes it as difficultly crystallizable, salifiable, and extremely poisonous; and details some experiments, from which it appears possessed of the same singular influence upon the circulating system as belongs to the plant itself. Other chemists have not succeeded in obtaining this alkali.

CINCHONIA.—The existence of a peculiar principle in *pale Peruvian Bark* was originally suggested by Dr. Duncan (*Nicholson's Journal*, vi. 225), and it was afterwards obtained, in a crystalline form, by Dr. Gomes; but its peculiar alkaloid properties, and a ready mode of procuring it, were first made known by Pelletier and Caventou. It may be obtained by several processes; but the following is, perhaps, the simplest, and, upon the whole, the most economical. A pound of the bruised bark (*cinchona lancifolia* of the Pharmacopœia) is boiled in about a gallon of water, acidulated by three fluid-drachms of sulphuric acid. A similar decoction is repeated with about half the quantity of liquid, and so on, till all the soluble matter is extracted. The decoctions are then mixed and strained, and powdered lime added, in a proportion somewhat greater than necessary to saturate the acid: the precipitate that ensues (a mixture chiefly of cinchonia and sulphate of lime) is collected, *carefully* dried, and boiled for some minutes

in strong alcohol, which is then decanted off, while hot, and fresh portions successively added for the repetition of the same operation, until it ceases to act upon the residue, which is now little else than sulphate of lime. The different alcoholic solutions are then put into a retort or still, and considerably evaporated; during which, and especially on cooling, cinchonia is deposited. When the whole is thus collected, the cinchonia must be redissolved in alcohol, and crystallized by its slow evaporation.

Cinchonia is thus obtained in the form of white semitransparent crystals, requiring about 2500 parts of water, at 212° , for their solution. They have little taste, but become intensely bitter upon the addition of almost any acid. They restore the blue colour of reddened litmus. They are sparingly soluble in cold alcohol, ether, and fixed oils: the hot solutions in these menstrua deposit crystals on cooling; and the alcoholic solution becomes milky when dropped into water. When cinchonia is heated in a small tube-retort, abundance of ammonia is evolved, easily recognized by its odour, action upon turmeric, and upon a glass rod moistened with muriatic acid: the odour of prussic acid may also be perceived; an oily matter, smelling like naphtha, distils over, and an abundant carbonaceous residue remains. The most remarkable circumstance attending this decomposition (provided the cinchonia be pure, and air carefully excluded), is the entire absence of all appearance of aqueous vapour, even when the products were made to pass through a considerable extent of cooled tube. This led me to suspect the absence of oxygen in cinchonia,—an opinion corroborated by its want of action upon potassium when heated with that metal in naphtha: the cinchonia, under these circumstances, readily dissolves in boiling naphtha, and again entirely separates as the solution cools, concreting into a radiated crystallized mass, in which the brilliant globules of potassium are disseminated. The mean result of my experiments, to determine the ultimate components of cinchonia, gives

Carbon	79.3
Nitrogen	13.6
Hydrogen	7.1

According to Pelletier and Dumas, the ultimate components are,

Carbon	76.97
Nitrogen	9.02
Hydrogen	6.22
Oxygen	7.79
					<hr/>
					100

The discrepancy of these results shews the necessity of further experiments; and I am not without hope, that the subject may fall under the investigation of Dr. Prout, whose practical skill enables him to meet the difficulties of these ultimate analyses in a more satisfactory manner than most of his contemporaries.

Cinchonia neutralizes the acids, and with many of them forms crystallizable compounds.

Muriate of Cinchonia forms acicular crystals, intensely bitter, and very soluble in water and alcohol.

Nitrate of Cinchonia is not crystallizable.

Sulphate of Cinchonia forms prismatic crystals, whose primitive form is a doubly-oblique rhombic prism. (*Ann. of Phil.*, N. S., vi. 375.) It requires 54 parts of water, at 60°, for its solution, but dissolves in 6.5 parts of alcohol, specific gravity 850. It is insoluble in ether. Exposed to heat, it phosphoresces, then fuses, reddens, and is decomposed. 100 parts of cinchonia require, for saturation, a quantity of dilute sulphuric acid, equivalent to 12.7 of real acid. Of the sulphate of cinchonia thus produced (and which I believe to be an anhydrous salt), 24 grains furnished, by decomposition with muriate of baryta, 8 grains of sulphate of baryta, equal to 2.72 of sulphuric acid; so that upon these data the number 315 will be the equivalent of cinchonia, that of sulphuric acid being 40.

Bisulphate of Cinchonia is a very soluble salt, which may be obtained from its concentrated solution in octoëdral crystals, with a rhombic base. It dissolves in half its weight of water, and in its own weight of alcohol, but is insoluble in ether. It effloresces in a warm atmosphere, and consists, according to Baup, of

1	proportional of cinchonia,
2	„ sulphuric acid,
8	„ water.

Phosphate of Cinchonia is very soluble and uncrystallizable.

Carbonate of Cinchonia is thrown down by the alkaline carbonates in the form of a white powder; and it is said that cinchonia absorbs carbonic acid from the atmosphere, but I have not remarked this.

Oxalate of Cinchonia is precipitable in the form of a white powder, soluble in boiling water, boiling alcohol, and in excess of acid.

Tartrate of Cinchonia resembles the oxalate, but is rather more soluble.

Gallate of Cinchonia falls in the form of a white powder, soluble in boiling water: this solution becomes opalescent as it cools, and deposits small crystalline grains.

Acetate of Cinchonia is difficultly crystallizable in small grains. The *binacetate* forms a gum-like mass.

QUINIA is a peculiar salifiable base, obtained from *yellow bark*, by a process similar to that for obtaining cinchonia; but it is not crystallizable; and, accordingly, when the precipitate by lime is digested in boiling alcohol, the solution deposits the quinia, upon evaporation, in the form of a viscid substance; which, if dried at 212° , assumes the appearance of resin; but if dried over sulphuric acid, in the vacuum of the air-pump, desiccates into a white pulverulent substance. It may be imperfectly crystallized by exposing its alcoholic solution to spontaneous evaporation in cold weather. If fused, and suffered to cool very slowly, it also concretes into an imperfectly crystalline mass. Quinia requires about 200 parts of boiling water for solution, and is more soluble in alcohol than cinchonia. Its taste is bitter, and intensely so when touched by an acid. It has been analyzed by Messrs. Pelletier and Dumas with the following result:—

Carbon	.	.	75.02	.	.	73.80
Nitrogen	.	.	8.05	.	.	13.00
Hydrogen	.	.	6.66	.	.	7.65
Oxygen	.	.	10.43	.	.	5.55
			<hr/>			<hr/>
			100			100

The second column contains the result of my own analysis; the two statements are, unfortunately, not sufficiently congruous to determine its atomic constitution.

The salts of quinia have an intensely bitter taste, and a

pearly lustre. Those which are soluble are precipitated by oxalic, tartaric, and gallic acids. From the experiments of Pelletier and Caventou, it appears that the equivalent of quinia is about 360.

Sulphate of Quinia is a salt in considerable commercial demand, in consequence of its extensive use as a febrifuge and tonic in medicine. It is made by digesting quinia in dilute sulphuric acid, which readily dissolves it; and the solution, when neutral, deposits small silky crystals, which, when pure, are perfectly white, difficultly soluble in cold water, much more soluble in hot water, soluble in alcohol, and sparingly so in ether. When heated it fuses, and then burns, leaving a carbonaceous residue, which may be completely burned away. This entire destructibility of the salt by heat enables us easily to ascertain in it the presence of certain impurities, which leave a residue *. The composition of this salt, as far as water of crystallization is concerned, has not been satisfactorily determined.

Bisulphate of Quinia.—When sulphate of quinia is triturated with its weight of dilute sulphuric acid, it concretes into a white magma, which dissolves upon the addition of more of the acid, and forms an intensely bitter and sourish solution.

When sulphuric acid, equal to an additional proportional, has been used, the solution yields, upon careful evaporation, long prismatic crystals of a salt much more soluble than the neutral sulphate, one part requiring not more than 12 of water at 60°. It is scarcely soluble in pure alcohol, and effloresces in the air. The crystals include a large proportion of water of crystallization; not less than 25 *per cent*.

Muriate of Quinia is more soluble than the sulphate; it forms pearly acicular crystals.

Hydriodate of Quinia is precipitated in the form of a white difficultly soluble powder.

Nitrate of Quinia is very difficultly crystallizable; when the solution is sufficiently evaporated, it separates in drops resembling oil, which concrete on cooling, and after some days

* It is liable to various adulterations, several of which, with the means of detecting them, have been pointed out by Mr. R. Phillips, (*Phil. Mag.*, February 1828.)

assume a decidedly crystalline appearance if allowed to remain in water, an appearance referable, according to Berzelius, to the gradual absorption of water of crystallization by the concrete, wax-like salt, which is an anhydrous nitrate.

Phosphate of Quinia is easily crystallizable, and soluble in water and alcohol.

Oxalate of Quinia is thrown down in the form of a white powder upon the addition of a neutral oxalate to the soluble salts of quinia. Its solution in boiling water deposits small shining crystals on cooling; or, if concentrated, concretes. It dissolves in alcohol, and in excess of oxalic acid: this latter solution furnishes crystals of the *binoxalate of quinia*.

Tartrate of Quinia much resembles the oxalate, but is somewhat more soluble.

Gallate of Quinia is precipitated in the form of a white powder, soluble in boiling water, in alcohol, and in excess of acid.

Acetate of Quinia forms silky congeries of crystals, difficultly soluble in cold, but readily soluble in hot water.

KINIC ACID.—This acid, which, in the varieties of Peruvian bark, is combined with cinchonia and quinia*, was discovered by Vauquelin, who pointed out a method of obtaining it nearly pure, and called it *Kinic Acid* (*Annales de Chimie*, lix.); but the term *Cinchonic Acid*, derived from the generic name of the plants which afford it, appears less exceptionable. This acid has also been examined by Pelletier and Caventou, and by MM. Henry and Plisson. (*Ann. de Chim.*, xxxv. 165.)

It may be obtained by boiling the bark, yellow bark, for instance, in water acidulated by sulphuric acid, filtering, and adding to the warm liquors, recently prepared, and moist hydrated oxide of lead, till they are perfectly neutralized, and acquire a yellow colour. The yellow liquid contains a little cinchonate of lead, a considerable quantity of cinchonate of lime, and either cinchonia or quinia, according as pale or yellow bark have been used, together with some colouring and

* The *pale bark* of commerce contains cinchonia, the *yellow bark* quinia, and the *red bark* (cinchonia oblongifolia) a mixture of cinchonia and quinia: these alkalis exist in the barks combined with kinic acid.

extractive matter. The precipitate thrown down consists of colouring matter in combination with oxide of lead, of sulphate of lead, some free quinia, but not any subcinchonate of lead.

The lead is separated from the yellow solution either by a little sulphuric acid, or by sulphuretted hydrogen. The liquor is filtered, and the quinia precipitated by a very slight excess of lime. What now remains dissolved is nearly pure cinchonate of lime; it is evaporated to the consistency of syrup, purified by a second crystallization, or by precipitation with alcohol, and decomposed by oxalic acid, added drop by drop, as Vauquelin recommends.

Cinchonic (kinic) acid furnishes a colourless aqueous solution, which, when concentrated, becomes yellow-brown. It is sour and slightly bitter, and difficultly crystallizable. Combined with soda, lime, magnesia, oxide of lead, quinia, and cinchonia, it forms definite salts, difficultly crystallizable, excepting that of lime. They are scarcely soluble in alcohol. When the aqueous solutions of its salts with cinchonia and quinia are evaporated in a water-bath, they assume the appearance of a yellow shining extract, which, slightly moistened and exposed to air, gradually concretes into a granular crystalline mass.

Cinchonic acid is soluble in about $2\frac{1}{2}$ parts of water at 50° : it dissolves in alcohol: its ultimate constituents are,

Carbon	34.115
Hydrogen	5.560
Oxygen	60.325
					<hr/>
					100

Section XX. OF THE PARTS OF PLANTS.

IN the preceding Sections the principal proximate components of vegetables have been described, and the composition of some of their detached parts has been adverted to; such of these as have not been previously noticed, and as have been

examined with any degree of precision, remain to be described in this Section, under the heads of

Roots.
Barks.
Woods.
Leaves.
Flowers.
Seeds.
Fruits.
Bulbs.
Lichens.
Fungi.

i. ROOTS.

a. Ipecacuanha.—This root is the produce of the *Calococca Ipecacuanha*. (LINNEAN *Trans.*, vi.) It has been examined by MM. Pelletier and Majendie, and an account of their researches is published by M. Robiquet, in the *Annales de Chim. et Phys.*, iv., 172. 100 parts of this root, deprived of the woody fibre which traverses its centre, afforded

Fatty matter	2
Emetine	14
Gum	16
Starch	18
Woody fibre	48
A trace of wax					
Loss	2
					<hr/>
					100

The means of separating the emetic principle have already been described. (See page 454.)

b. Valerian, the root of the *Valeriana officinalis*, has been examined by Trommsdorf. (*Annales de Chimie*, lxx.) The recent root loses about three-fourths its weight in drying. It affords, when distilled with water, an aromatic volatile oil; it also contains starch, gum, resin, and extractive.

c. Turmeric is the root of the *Curcuma longa*, a plant cultivated in the East Indies, and used as a condiment, especially in *Curry powder*. Digested in water or alcohol, it furnishes a large proportion of yellow colouring matter, which would be very useful to the dyer, could it be rendered permanent. Most of the acids render it paler, and the alkalis change it to a deep

brick-red; hence its use as a test of the presence of alkaline matter. It is also reddened by boracic acid, and by muriatic acid gas. Some of the peculiarities of the colouring principle of turmeric have been noticed by M. Desfosses (*Ann. de Chim. et Phys.* xvi. 75), and by Mr. Faraday. (*Quarterly Journal*, xi. 403.)

d. Madder is the root of the *Rubia Tinctorum*, and is an article of great importance in dyeing; it grows wild in most parts of the south of Europe, and is largely cultivated in some parts of Holland and the Levant; its red colour is apt to be injured by drying, a process requiring much caution. Good madder has a strong and peculiar smell; it exhibits, when cut, a cortical and a woody part of a red colour, intermixed in the former with yellow spots. The red portion is most soluble. A peculiar substance, obtained from madder, has already been noticed under the name of *Alyzarine*. (see p. 475.) AIKIN'S *Dictionary*—Art. DYEING. BERTHOLLET, *Elem. de Teinture*, ii.

e. Rhubarb is the root of the *Rheum palmatum*, largely cultivated in the northern parts of China; its colour is brown, with streaks of red and white. The following are the component parts, separable from the finest kinds of Turkey rhubarb. (BRANDE, *Quarterly Journal of Science and the Arts*, x. 291.)

Water	8.2
Gum	31.0
Resin	10.0
Extract, tan, and gallic acid	26.0
Phosphate of lime	2.0
Malate of lime	6.5
Woody fibre	16.3
	<hr/>
	100

Liquorice, the root of the *Glycyrrhiza glabra*, has been examined by M. Robiquet, who found in it the following substances (*Annales de Chimie*, lxx.) :—

- i. Starch.
- ii. Gluten.
- iii. Liquorice sugar.
- iv. Phosphate and malate of lime and magnesia.
- v. An acrid oil.
- vi. A crystallizable substance resembling asparagin.
- vii. Woody fibre.

The sugar is soluble in water and in alcohol, but not convertible into alcohol by fermentation, nor into oxalic acid by the action of nitric acid.

Jalap, the root of the *Convolvulus Jalappa*, is employed in medicine as a cathartic. It is imported from South America. It has not been submitted to any accurate chemical analysis, but its activity is generally regarded as chiefly resident in its resin. The finest and densest jalap affords about 12 *per cent.* of resin, when digested in alcohol; water takes up about 30 or 35 *per cent.* of the remainder, and the residue appears to be inert woody fibre.

Gentian is the root of the *Gentiana lutea*; according to Mr. Henry (*Annals of Philosophy*, xvi. 89), it contains the following substances:

- i. A substance resembling bird-lime.
- ii. A resin combined with oil, which gives to gentian its peculiar odour.
- iii. A bitter extractive principle.
- iv. Gum and colouring matter.
- v. Phosphate of lime?

ii. BARKS.

a. Cinchona.—The varieties of Peruvian bark have been examined by MM. Pelletier and Caventou. In the *cinchona lancifolia*, or *pale bark*, they found the following constituent parts:—

- i. Cinchonina, combined with kinic acid.
- ii. Green fatty matter.
- iii. Red and yellow colouring matter.
- v. Tannin.
- v. Kinat of lime.
- vi. Gum
- vii. Starch.
- viii. Lignin.

b. Cascarilla, the bark of the *Croton Eleutheria*, contains, according to Trommsdorff (*Annales de Chimie*, xxii.),

	Parts.
Mucilage and bitter principle	864
Resin	688
Volatile oil	72
Water	48
Woody fibre	3024
	<hr/> 4696

c. The bark of the *horse chestnut* (*Æsculus hippocastanum*) has been partially examined by M. Henry. (*Annales de Chimie*, lxxvii.) It appears to contain scarcely any resin; water and diluted alcohol dissolve nearly the whole of its soluble contents, which are chiefly extractive and mucilage. Tincture of galls does not render its infusion turbid; it does not, therefore, probably contain the peculiar substances discovered in Peruvian bark.

The bark of the *Daphne Alpina* contains, according to Vauquelin, a peculiar bitter principle, which he has called *Daphnin*.

iii. WOODS.

a. *Brazil Wood* is the produce of the *Cæsalpina crista*, growing in Brazil, in the Isle of France, Japan, and other countries: the wood is hard and heavy, and though pale when recent, it acquires a deep red colour by exposure. Digested in water, it affords a fine red infusion, of a sweetish flavour; the residue, which appears nearly black, imparts much of its colour to alkaline liquors. With alcohol, it gives a deep red tincture; alkalis and soap convert its red colour to a fine purple: hence paper, tinged with Brazil wood, is sometimes used as a test for alkalis; acids render it yellow; alum produces a fine crimson lake with infusion of Brazil wood; muriate of tin forms with it a crimson precipitate, bordering on purple; the salts of iron give a dingy purple colour. Sulphuretted hydrogen destroys the colour of infusion of Brazil wood, but it re-appears on expelling the gas.—CHEVREUL, *Annales de Chimie*, lxvi.

b. *Red Sandal*, or *Saunders*, is the wood of the *Pterocarpus santalinus*, a native of several parts of India. Its deep red colouring matter is insoluble in water, but readily soluble in alcohol; it is chiefly employed for colouring a few pharmaceutical tinctures. The insolubility of its colouring principle in water furnishes a ready mode of distinguishing between it and Brazil wood; and its solubility in alcohol renders it probable that it is of a resinous nature.

c. *Logwood*, the produce of the *Hæmatoxylon campechianum*, has already been noticed as containing a peculiar colouring prin-

ciple. (See page 452.) It imparts a fine purple or crimson colour to pure water, but its tint is altered by the slightest metallic impregnation; alkalis deepen it, and acids render it paler; alum forms with it a violet-coloured lake; sulphate of iron renders the infusion of logwood deep purple, or nearly black; sulphate of copper and acetate of lead throw down brown and purple precipitates; and muriate of tin precipitates the whole of the colouring matter in the form of a purple compound. The colours which logwood produces are for the most part very perishable.—BANCROFT, *on Permanent Colours*, ii. 338. CHEVREUL, *Annales de Chimie*, lxvi. 254.

iv. LEAVES.

a. Senna.—According to Lagrange (*Annales de Chimie*, xxvi.), the leaves of the *Cassia senna* are characterized by containing a peculiar extractive principle, which by long boiling passes into a resinous substance, in consequence of absorbing oxygen: they also contain a resin which resists the action of water, and is soluble in alcohol; the whole of the soluble matter amounts to about one-third the weight of the senna. In the *London Medical Repository*, vol. xv., 169, the effects of various re-agents on infusion of senna are detailed by Mr. Batley.

b. Nightshade.—The leaves of the *Atropa Belladonna* contain, according to Vauquelin (*Annales de Chimie*, lxxii.),

- i. Vegetable albumen.
- ii. A bitter narcotic principle.
- iii. Nitrate, muriate, sulphate, binoxalate, and acetate of potassa.

Dr. Brandes has announced the existence of a new vegetable alkali in this plant, which he calls *atropia*. (See page 451.)

c. Hyoscyamus Niger, or Henbane.—In the leaves of this plant Dr. Brandes states that he has also ascertained the presence of a peculiar, and highly poisonous, salifiable base which he calls *hyoscyama*. (See page 452.)

Tea Leaves.—Professor Pfaff informs me that a peculiar salifiable base has been discovered in green tea, but I am not acquainted with the process for its separation. Some years ago I examined the varieties of tea in common use (*Quarterly Journal*, O. S., xii. 201), and found that the quantity of

astringent matter precipitable by gelatine is somewhat greater in green than in black tea, though the excess is by no means so great as the comparative flavours of the two would lead one to expect. The entire quantity of soluble matter is also greater in green than in black tea, but the extractive matter not precipitable by gelatine is greater in the latter.

The following table shows the respective quantities of soluble matter in water and in alcohol, the weight of the precipitate by isinglass, and the proportion of inert woody fibre in green and black tea of various prices. It is given, not as throwing any important light upon the cause of the different qualities and effects of tea, but as containing the results of actual experiments. It will be remarked, that when tea leaves have been exhausted by water repeatedly affused, alcohol is still capable of extracting a considerable quantity of soluble matter: the alcoholic extract, infused in boiling water, furnishes a liquid which smells and tastes strongly of tea, and which, were it not for the expense of the solvent, and the trouble attending its separation, might perhaps be profitably employed.

One hundred parts of Tea.		Soluble in Water.	Soluble in Alcohol.	Precipitate with Jelly.	Inert residue.
Green hyson	14s. per lb.	41	44	31	56
"	12s. "	34	43	29	57
"	10s. "	36	43	26	57
"	8s. "	36	42	25	58
"	7s. "	31	41	24	57
Black souchong	12s. "	35	36	28	64
"	10s. "	34	37	28	63
"	8s. "	37	35	28	63
"	7s. "	36	35	24	64
"	6s. "	35	31	23	65

V. FLOWERS.

The colouring matter of most flowers is extremely fugitive, and is generally much changed by mere exsiccation. They usually communicate their colour to water: the infusion of blue flowers is generally reddened by acids, and changed to green or yellow by alkalis; that of yellow flowers is made paler by acids, and alkalis render it brown: the red infusion of many flowers is exalted in tint by acids; and changed to purple, and in some instances to green, by alkalis.

It is probable that one and the same principle gives colour to

several of the blue and red flowers, but that the presence of acid in the latter produces the red ; the petals of the red rose, triturated with a little carbonate of lime and water, give a blue liquor ; alkalis render it green, and acids restore the red.

A colouring matter, analogous to that of the violet, exists in the petals of red clover, in the red tips of those of the common daisy, of the blue hyacinth, the hollyhock, lavender, in the inner leaves of the artichoke, and in numerous other flowers ; reddened by an acid, it colours the skin of several plums, and the petals of the scarlet geranium and pomegranate. Some flowers which are red, become blue by merely bruising them ; this is also the case with the colouring matter of red cabbage leaves, and of the rind of the long radish. Mr. Smithson has suggested that the reddening acid is in these cases the carbonic, which escapes on the rupture of the vessels which inclose it.

The petals of the common *corn-poppy*, rubbed upon paper, give a purple stain, little altered by ammonia or carbonate of soda, but made green by caustic potassa. The infusion of poppy-petals in very dilute muriatic acid, is florid red ; chalk added, renders it of the colour of port wine ; carbonate of soda in excess gives the same colour, but excess of potassa changes it to green and yellow. The expressed juice of the black mulberry possesses nearly the same properties.—SMITHSON, *Phil. Trans.* 1818, 110.

The flowers of the *carthamus tinctorius*, or *safflower*, cultivated chiefly in Spain and the Levant, contain a yellow colouring matter, easily soluble in water, and a red, soluble in alcohol and weak alkaline liquors ; the latter only is employed. *Rouge* is the red colouring matter of the *carthamus*, obtained by digesting the washed flowers in solution of carbonate of soda, and adding lemon juice, which throws it down in the form of a fine powder, which is dried and mixed with a portion of powdered talc ; *carthamus* is also used for dyeing silk. The details of the analysis of *carthamus* will be found in the *Essays* of Dufour and Marchais.—*Annales de Chimie*, xlviii.

The cones of the *Humulus lupulus*, or *hops*, have been examined by MM. Payen and Chevaliér. (*Quarterly Journal*, xiii. 402.) Their active ingredients are a narcotic essential oil, a yellow resin, and a bitter principle possessed of peculiar

medical qualities, which has been called *Lupulin*. These substances are chiefly confined to the yellow grains scattered over the scales of the cones.

vi. SEEDS.

Starch is an essential component of the greater number of seeds, and it is generally united in them with a variable portion of mucilage, gluten, and often of fixed and of volatile oil. The component parts of wheat-flour, and of several esculent grains, have already been stated, and a variety of curious details respecting them will be found in EINHOF's *Papers*, in GEHLEN's *Journal*.

Sir H. Davy has also examined a number of seeds, with a view to determine their relative nutritive powers; the results of his experiments are seen in the table at page 449.

Almonds, the seed of the *amygdalus communis*, consist of an albuminous substance and oil; the latter may be obtained by expression, five pounds yielding about two pounds of cold drawn oil, and nearly two and a half when aided by heat. The bitter almond affords, by pressure, an oil analogous to that from the former; but if the expressed cake be distilled with water, a portion of volatile oil, eminently poisonous, and smelling strongly of the almond, is obtained; this oil is used as a flavouring material by confectioners, and by the manufacturers of noyau. It contains hydrocyanic acid, as may be shown by digesting it with red oxide of mercury, which forms cyanuret of mercury. In the *Philosophical Transactions* for 1811, Mr. Brodie has detailed a variety of experiments illustrative of its action as a poison, in which, as well as from its odour, it appears identical nearly with hydrocyanic acid. Peach and laurel leaves, and the seeds of several other fruits, also contain hydrocyanic acid.

Lentiles, the seed of the *ervum lens*, contain, according to Einhoff, in 3840 parts,

Woody fibre	720
Albumen	44
Earthy phosphates	22
Extractive, soluble in alcohol	120
Gum	230
Starch	1260
Gluten	1433
Loss	11
					<hr/>
					3840

The seeds of the *white lupine* (*lupinus albus*) contain, according to Foureroy and Vauquelin (*Ann. du Muséum*, No. xxxvi.), gluten, and a green acrid oil, with a considerable portion of phosphate of lime and magnesia, but no starch or sugar.

Coffee, the seed of the *Coffea Arabica*, has been examined both in its raw and roasted state. From 64 parts of raw coffee, Cadet (*Ann. de Chim.*, lviii.) obtained

Gum	8.
Resin and bitter extract	2.0
Gallic acid	3.5
Insoluble matter	43.5
Loss, including a trace of albumen	7.0
						<hr/> 64.

Hermann has given the following comparative analysis of coffee from the Levant and from Martinique (CRELL's *Annals*, ii.), the results of which differ much from those of Cadet:—

	Levant.	Martinique.
Resin	74	68
Extractive	320	310
Gum	130	144
Fibrous matter	1335	1386
Loss	61	12
<hr/> 1920		<hr/> 1920

When coffee is roasted, it undergoes a peculiar change of composition, attended by the formation of tan, and of a fragrant and aromatic principle. There is also produced a considerable portion of a brown volatile matter, which, when purified by a second sublimation, yields acicular crystals of a brown colour. These may be purified by solution in water, to which powdered charcoal is added; and when recrystallized, form beautiful groups of brilliant silky needles. Robiquet, who first described this substance in 1821, regarded it as a salifiable base; but it does not form definite combinations with the acids. According to Pelletier and Dumas, its ultimate components are,

Carbon	46.51
Nitrogen	21.54
Hydrogen	4.81
Oxygen	27.14
						<hr/> 100

The proportion of nitrogen is very large for a vegetable product. It has been termed *caffeine*, and is said to be exhilarating in doses of four or five grains. It has a bitterish flavour.

Pepper.—The seed of the *piper nigrum* has not been satisfactorily analyzed: it imparts its acrimony to alcohol and to water: it contains a species of volatile oil, with starch and extractive matter.—NICHOLSON'S *Journal*, ii.

M. Pelletier has given the term *piperin* to a vegetable principle which he obtained from black pepper by the following process:—It was digested repeatedly in alcohol, and the solution evaporated until a fatty resinous matter was left; which, washed with warm water, was green, and of a hot burning taste; it was readily soluble in alcohol, less so in ether; and converted to a fine scarlet colour by sulphuric acid. Its alcoholic solution, being left for some days, deposited crystals, which were purified by solution in ether; they were then obtained in white four-sided prisms, and with little taste, insoluble in cold water, very soluble in alcohol, and less so in ether.

The fatty matter is solid at 32°; it is bitter and acrid, and soluble in alcohol and ether.

Mustard.—The seed of the *sinapis nigra* derives its acrimony from a volatile oil; it also contains a tasteless fixed oil, albumen, gum, and traces of sulphur and earthy salts.

The seeds of the *lycopodium clavatum*, or *common club moss*, have been analyzed by Bucholz. (GEHLEN'S *Journal*, vi.) From 1000 parts he obtained,

Fixed oil	60
Sugar	30
Mucilage	15
Insoluble residue	895
						<hr/> 1900

This seed has the appearance of a fine yellow powder, which deflagrates when projected into the flame of a candle; it is used in theatres to imitate lightning; and the German apothecaries employ it to prevent the adhesion of pills.

Annotta is the produce of the *bixa orellana*, a tree cultivated in various parts of America. When the capsules are ripe, the

seeds are bruised and steeped for several weeks in water, until converted into a pulp, which is allowed to putrefy; and, being diffused through a fresh portion of water, is heated till a scum rises, which is successively removed as it forms, and being carefully dried, is made up into cakes, and wrapped in palm leaves for exportation.

Annotta is soluble in water and alcohol; the solutions have a disagreeable smell, and are of an orange colour; alkalis render it more soluble, and increase its colour: alum and the acids separate it from its solutions in the form of a yellow sediment: it is used for dyeing silk and colouring cheese.

vii. FRUITS.

The acid matter contained in fruits is either the tartaric, oxalic, citric, or malic; or a mixture of two or more of them; but the nature and proportion of the acid varies at different periods of their growth; gluten and starch are found in some fruits, and a gelatinizing substance, lately called *Pectic Acid*, which has sometimes been regarded as identical with animal jelly, but which is probably a compound of gum, and one or more vegetable acids. (See page 428.)

Most of our common fruits also contain sugar; and it exists in all those the juice of which is susceptible of vinous fermentation. In some fruits, the quantity of sugar is increased by mashing and exposure to air; this is remarkably the case with some of the rough-flavoured apples used for cyder, the pulp of which becomes brown, and at the same time sweet by a few hours' exposure.

The colouring matter of fruits seems, in most cases, to bear a strong resemblance to that of flowers. The red juice of the mulberry was found to exhibit the same characters as the colouring principle of the wild poppy; carbonated alkalis render it blue, but caustic potassa changes it to green and yellow: the juice of red currants, cherries, elder berries, and privet berries, and the skin of the buckthorn berry, appear to contain a similar colouring principle.

The unripe berries of the buckthorn furnish a juice, which, when inspissated, is known under the name of *sap-green*. It

is soluble in water, and rendered yellow by carbonate of soda and caustic potassa; the acids redden it, and carbonate of lime restores it to green, which is therefore probably the proper colour of the substance. (SMITHSON, *Phil. Trans.*, 1818, p. 116.)

The fruit of the *wild cucumber* (*cucumis elaterium*) furnishes a very acrid juice, which deposits the powerful cathartic known under the name of *elaterium*. This substance occurs in commerce in thin cakes of a greenish colour and bitter taste; it derives its cathartic powers from a small portion of a very active principle, which Dr. Paris has called *Elatin* (*Pharmacologia*, 223, 3d Edit.): from 10 grains of elaterium, he obtained,

Water	0.4
Extractive	2.6
Fecula	2.8
Gluten	0.5
Woody matter	2.5
Elatin	}	.	.	.	1.2
Bitter principle		.	.	.	
					<hr/> 10

viii. BULBS.

The *potato*, which is the bulbous root of the *solanum tuberosum*, has been examined by Dr. Pearson and by M. Einhoff; from 100 parts, the latter chemist obtained,

Starchy matter	.	.	.	22
Albumen and mucilage	.	.	.	5.4
				<hr/> 27.4

The average quantity of nutritive matter contained in the potato, amounts to about one-fourth its weight. When potatoes become sweet by exposure to frost, a portion of the mucilage passes into the state of sugar, for Einhoff found the quantity of starch undiminished. (See page 444.)

Garlic, or the bulbous root of the *allium sativum*, has been examined by Cadet.—(*Annales de Chim.*, lix.) It loses, by drying, about two-thirds of its weight; its juice is viscid, and very slightly sour; it yields coagulated albumen when heated; and when distilled with water furnishes an acrid oil, having a strong odour of garlic.

The bulb of the *Allium Cepa*, or *Onion*, has been analyzed by Fourcroy and Vauquelin. (*Ann. de Chim.*, lxxv.) The juice of this root, when exposed to a temperature of about 70° , forms a quantity of vinegar, and deposits a sediment having the characters of gluten, combined with oil and sulphur. In the acetous solution is contained a substance having the properties of manna, and which is probably a product of the fermentation, for none could be detected in the recent juice.

Squill, the bulbous root of the *Scilla maritima*, contains, according to Vogel, (*Annales de Chim.*, lxxxiv.) a peculiar bitter principle, which he terms *Scillitin*, combined with gum, and a considerable portion of tannin.

ix. LICHENS.

There are several Lichens which abound in colouring matter, of these the most remarkable is the *Lichen roccella*, which grows in the south of France, and in the Canary Islands, and which affords the beautiful but perishable blue called *litmus*, *archil*, or *turnsole*. The moss is dried, powdered, mixed with pearl-ash and urine, and allowed to ferment, during which it becomes red, and then blue; in this state it is mixed with carbonate of potassa and chalk, and dried. It is used for dyeing silk and ribands, and by the chemist as a most delicate test of acids, which it indicates by passing from blue to red; the blue colour is restored by alkalis, which do not render it green. *Cudbear* appears to be a similar preparation of the *lichen tartareus*. —BANCROFT on Colours, i. 300.

Mr. Smithson has thrown some doubt upon the use of alkalis in the preparation of litmus, for he found its tincture produce no change on solutions of muriate of lime, nitrate of lead, muriate of platinum, and oxalate of potassa; he at the same time suggests the idea of its being a compound of a vegetable principle with potassa.—*Phil. Trans.*, 1818, p. 112.

The *Lichen Islandicus*, or *Iceland Moss*, has been subjected to analysis by Berzelius. (*Ann. de Chim.*, xc.) He obtained from it the following substances:—

Syrup	3.6
Bitartrate of potassa	}	.	.	.	1.9
Tartrate of lime		.	.	.	
Phosphate of lime		.	.	.	
Bitter principle	3.0
Wax	1.6
Gum	3.7
Colouring extract	7.0
Starch	44.6
Insoluble starchy matter	36.6
					<hr/> 102

X. FUNGI, OR MUSHROOMS.

M. Braconnot, who has lately examined many fungi with minute attention, has given the name *fungin* to the insoluble spongy portion which they contain, and which in many respects resembles lignin; he has also detected in them two peculiar acids, which he terms *fungic acid* and *boletic acid*; the method of extracting which has been above described. A peculiar fatty matter, or adipocere, has been found by Vauquelin and Braconnot, in several of the fungi; an albuminous substance, and salts, some of which are boletates and fungates, have also been detected in them, but the analyses are too abstruse, and the results too complicated, to be regarded as perfectly satisfactory.—*Ann. de Chim.*, lxxix., lxxxv., &c.

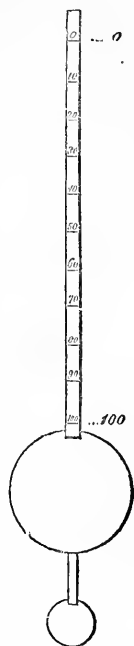
Section XXI. PHENOMENA AND PRODUCTS OF FERMENTATION.

THE term *fermentation* is employed to signify the spontaneous changes which certain vegetable solutions undergo, placed under certain circumstances, and which terminate either in the production of an intoxicating liquor, or of vinegar; the former termination constituting *vinous*, the latter *acetous* fermentation.

The principal substance concerned in vinous fermentation is sugar; and no vegetable juice can be made to undergo the process perfectly, which does not contain it in a sensible quantity.

In the production of beer, the sugar is derived from the malt ; in that of wine, from the juice of the grape.

In the manufacture of *beer*, the malt is ground and infused in the *mash-tun*, in rather more than its bulk of water, of the temperature of 160° or 180° . Here the mixture is stirred for a few hours ; the liquor is then run off, and more water added, until the malt is exhausted. These infusions are called *wort*, and its principal contents are *saccharine matter*, *starch*, *mucilage*, and a small quantity of *gluten*. The strength of the wort is adjusted by its specific gravity, which is usually found by an instrument not quite correctly called a *saccharometer*, since it is influenced by all the contents of the wort, and not by the sugar only. It is a brass instrument, of the shape shown in the margin, so adjusted in weight as to sink to the point marked 0° , in distilled water, at the temperature of 70° , and when immersed in a liquor of the same temperature, and of the specific gravity of 1.100, it is buoyed up to the mark 100, just above the bulb. The intermediate space is divided into 100 equal parts, and, consequently, will indicate intermediate degrees of specific gravity. This is the most useful form of the instrument, though not that in common use. The specific gravity of the wort for ale is usually about 1.090 to 1.100, and for table-beer from 1.020 to 1.030.



The wort is next boiled with hops, amounting, upon the average, to one-twentieth the weight of the malt, their use being to cover the sweetness of the liquor by their aromatic bitter, and to diminish its tendency to acidify. The liquor is then thrown into large, but very shallow, vessels, or *coolers*, where it is cooled to about 50° , as quickly as possible ; it is then suffered to run into the *fermenting vat*, having been previously mixed with a proper quantity of *yeast*, which accelerates fermentation, apparently by virtue of the gluten which it contains.

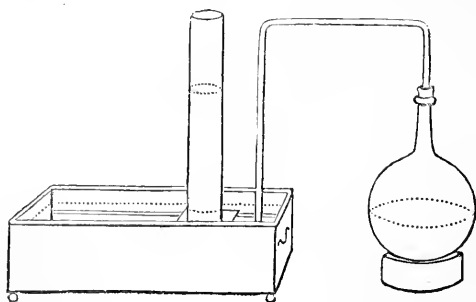
In the fermenting vessel, the different substances held in solution in the liquor begin to act upon each other ; an in-

testine motion ensues, the temperature of the liquor increases, carbonic acid escapes in large quantities; at length this evolution of gas ceases, the liquor becomes quiet and clear, and it has now lost much of its sweetness, has diminished in specific gravity, acquired a new flavour, and become intoxicating.

The distillers prepare a liquor, called *wash*, for the express purpose of producing from it ardent spirits; instead of brewing this from pure malt, they chiefly employ raw grain, mixed with a small quantity only of malted grain; the water employed in the mash-tun is of a lower temperature than that requisite in brewing, and the mashing longer continued; by which it would appear that a part of the starch of the barley is rendered into a kind of saccharine matter. The wort is afterwards fermented with yeast.

Wine is principally procured from the juice of the grape, and some other saccharine and mucilaginous juices of fruits. The principal substances held in solution in grape juice are, *sugar, gum, gluten, and bitartrate of potassa*. It easily ferments spontaneously at temperatures between 60° and 80° , and the phenomena it gives rise to closely resemble those of the wort with yeast. After the operation, its specific gravity is much diminished, its flavour changed, and it has acquired intoxicating powers.

If a mixture of 1 part of sugar, 4 or 5 of water, and a little yeast, be placed in a due temperature, it also soon begins to ferment, and gives rise to the same products as wort or grape-juice; and, as the free admission of air is not necessary to vinous fermentation, its results may easily be examined by suffering the process to go on in the following apparatus;



consisting of a matrass containing the fermenting mixture, with a bent tube issuing from it, and passing into an inverted jar standing in water.

It will thus be found that the only gaseous product is carbonic acid ; and, consequently, that carbon and oxygen are the principles which the saccharine matter loses during the process.

When any of the above-mentioned fermented liquors are distilled, they afford a *spirituous liquor* ; that from wine is termed *brandy* ; from the fermented juice of the sugar-cane we obtain *rum* ; and from wash, *malt spirit* ; and these spirituous liquors, by re-distillation, furnish *spirit of wine*, *ardent spirit*, or *alcohol*.

The different fermented liquors furnish very different proportions of alcohol, and it has been sometimes supposed that it does not pre-exist to the amount in which it is obtained by distillation (FABRONI, *Ann. de Chim.*, xxx.): but some experiments which I made upon the subject, in 1811 and 1813, and which are printed in the *Philosophical Transactions* for those years, tend to show that is a real educt, and not formed by the action of heat upon the elements existing in the fermented liquor. The following table exhibits the proportion of alcohol, specific gravity .825 at 60°, by measure, existing in 100 parts of several kinds of wine and other liquors :

					Proportion of Spirit per Cent. by measure.
1.	Lissa	.	.	.	26.47
	Ditto	.	.	.	24.35
			Average	.	25.41
2.	Raisin wine	.	.	.	26.40
	Ditto	.	.	.	25.77
	Ditto	.	.	.	23.20
			Average	.	25.12
3.	Marsala	.	.	.	26.03
	Ditto	.	.	.	25.05
			Average	.	25.09
4.	Port	.	.	.	25.83
	Ditto	.	.	.	24.29
	Ditto	.	.	.	23.71
	Ditto	.	.	.	23.39
	Ditto	.	.	.	22.30
	Ditto	.	.	.	21.40
	Ditto	.	.	.	19.00
			Average	.	22.96

					Proportion of Spirit per Cent. by Measure.
5.	Madeira	.	.	.	24.42
	Ditto	.	.	.	23.93
	Ditto (Sercial)	.	.	.	21.40
	Ditto	.	.	.	19.24
			Average	.	22.27
6.	Currant wine	.	.	.	20.55
7.	Sherry	.	.	.	19.81
	Ditto	.	.	.	19.83
	Ditto	.	.	.	18.79
	Ditto	.	.	.	18.25
			Average	.	19.17
8.	Teneriffe	.	.	.	19.79
9.	Colares	.	.	.	19.75
10.	Lachryma Christi	.	.	.	19.70
11.	Constantia, white	.	.	.	19.75
12.	Ditto, red	.	.	.	18.92
13.	Lisbon	.	.	.	18.94
14.	Malaga	.	.	.	18.94
15.	Bucellas	.	.	.	18.49
16.	Red Maderia	.	.	.	22.30
	Ditto	.	.	.	18.40
			Average	.	20.35
17.	Cape Muschat	.	.	.	18.25
18.	Cape Madeira	.	.	.	22.94
	Ditto	.	.	.	20.50
	Ditto	.	.	.	18.11
			Average	.	20.51
19.	Grape wine	.	.	.	18.11
20.	Calcavella	.	.	.	19.20
	Ditto	.	.	.	18.10
			Average	.	18.65
21.	Vidonia	.	.	.	19.25
22.	Alba Flora	.	.	.	17.26
23.	Malaga	.	.	.	17.26
24.	White Hermitage	.	.	.	17.43
25.	Rousillon	.	.	.	19.00
	Ditto	.	.	.	17.26
			Average	.	18.13
26.	Claret	.	.	.	17.11
	Ditto	.	.	.	16.32
	Ditto	.	.	.	14.03
	Ditto	.	.	.	12.91
			Average	.	15.10
27.	Zante	.	.	.	17.05
28.	Malmsey Madeira	.	.	.	16.40
29.	Lunel	.	.	.	15.52
30.	Sheraaz	.	.	.	15.52
31.	Syracuse	.	.	.	15.28
32.	Sauterne	.	.	.	14.22

						Proportion of Spirit <i>per Cent. by Measure.</i>
33.	Burgundy	16.60
	Ditto	15.22
	Ditto	14.53
	Ditto	11.95
				Average	.	14.57
34.	Hock	14.37
	Ditto	13.00
	Ditto (old in cask)	8.88
				Average	.	12.08
35.	Nice	14.63
36.	Barsac	13.86
37.	Tent	13.30
38.	Champagne (still)	13.80
	Ditto (sparkling)	12.80
	Ditto (red)	12.56
	Ditto (ditto)	11.30
				Average	.	12.61
39.	Red Hermitage	12.32
40.	Vin de Grave	13.94
	Ditto	12.80
				Average	.	13.37
41.	Frontignac (Rivesalte)	12.79
42.	Cote Rotie	12.32
43.	Gooseberry wine	11.84
44.	Orange wine—average of six samples made by a London manufacturer					11.26
45.	Tokay	9.88
46.	Elder wine	8.79
47.	Cider, highest average	9.87
	Ditto, lowest ditto	5.21
48.	Perry, average of four samples	7.26
49.	Mead	7.32
50.	Ale (Burton)	8.88
	Ditto (Edinburgh)	6.20
	Ditto (Dorchester)	5.56
				Average	.	6.87
51.	Brown Stout	6.80
52.	London Porter (average)	4.20
53.	Ditto Small Beer (ditto)	1.28
54.	Brandy	53.39
55.	Rum	53.68
56.	Gin	57.60
57.	Scotch Whiskey	54.32
58.	Irish ditto	53.90

The wines employed in the experiments upon which the preceding table is founded, were selected with all possible caution as to purity and quality; a given measure of each (saturated, when necessary, with lime or potassa) was carefully

distilled nearly to dryness, and the bulk of the distilled product was exactly made equal to that of the original wine by the addition of distilled water. After twenty-four hours its specific gravity was determined, and thence the quantity of alcohol, by reference to Mr. Gilpin's tables. The management of this and similar distillations is well described by Mr. Faraday. (*Manip.* p. 212.)

The principle upon which the intoxicating properties of fermented liquors depends, and which exists in ardent spirits, is in its purest form called *alcohol*. It may be obtained by distilling the *rectified spirit of wine* of commerce with substances having a strong attraction for water; such, for instance, as carbonate of potassa, quicklime, chloride of calcium, &c.

When carbonate of potassa is used, it should be added warm to the spirit, and the mixture well stirred or shaken; such quantity is requisite as to leave a small portion of the salt undissolved. Upon standing at rest, the mixture soon separates into two portions: the uppermost is the alcohol; the lower, an aqueous solution of the carbonate: the alcoholic portion being carefully decanted from the residue, is to be put into a retort, and about three-fourths of it distilled over at a moderate heat into a cooled receiver. Dry chloride of calcium may be used in the same way as the carbonate of potassa, and is a very effective agent for the separation of the water. Gay-Lussac recommends lime or baryta (*Ann. de Chim.*, lxxxvi.); the former may be used with the greatest advantage and economy: the spirit should be shaken up with a sufficient quantity of finely-powdered lime, and left some days in contact with it; it should then be poured off and cautiously distilled. When spirit of wine is put into a bladder, or into a glass vessel with a wide mouth, tied over with bladder, it is found that the aqueous vapour penetrates the animal membrane, in preference to the alcoholic vapour, so that the spirit, by spontaneous evaporation, becomes thus concentrated within the bladder or vessel; spirit of the specific gravity of .867, was thus easily reduced to .817. (*Quarterly Journal*, viii. 381, and xviii. 180.) But this, though a curious experiment, and well adapted to strengthen common spirit, is not adapted to the preparation of pure alcohol. Upon somewhat the same principle, Mr. Graham, of Glasgow, has ingeniously proposed to concen-

trate alcohol as follows. (*Edinb. Phil. Trans.*, 1828.) A shallow vessel is sprinkled over with coarsely-powdered quicklime, and a smaller one containing spirit of wine is placed just above it; both are covered by a proper bell-glass, upon the plate of an air-pump, and the air exhausted till the alcohol begins to boil. Of the vapour which rises, the lime only absorbs the aqueous part, and as water cannot remain under these circumstances in alcohol, unless covered by an atmosphere of its own vapour, it continues in uninterrupted evaporation, whilst the escape of alcohol is prevented by the pressure of its own unabsorbed vapour. If sulphuric acid be substituted as the absorbent instead of quicklime, it absorbs both vapours, and the whole of the spirit evaporates.

Alcohol thus obtained, by any of these processes, is a limpid, colourless liquid, of an agreeable smell, and a strong pungent flavour. It is considerably lighter than water. Its specific gravity varies with its purity; the purest obtained by rectification over muriate of lime being .791; as it usually occurs it is .820, at 60°. If rendered as pure as possible by *simple* distillation, it can scarcely be obtained of a lower specific gravity than .825, at 60°. The London Pharmacopœia states rectified spirit to have the specific gravity of .835. Alcohol is sufficiently volatile to produce considerable cold during evaporation, though in this respect much inferior to ether. The degree of cold is proportional to the purity of the alcohol. (*Quarterly Journal*, x. 187.)

Alcohol has never been frozen, and consequently is particularly useful in the construction of thermometers intended to measure intense degrees of cold. When of a specific gravity of .825, it boils at the temperature of 176°, the barometrical pressure being 30 inches. When its specific gravity is as low as .800 its boiling point is 173.5°; and when raised by the addition of water to a specific gravity of .900, its boiling point, according to Dalton, is elevated to 182°. A table of the boiling points of various mixtures of alcohol and water, founded on M. Groening's experiments, is given in the *Annals of Philosophy*, N. S., v. 313. In the vacuum of an air-pump alcohol boils at common temperatures. The specific gravity of the vapour of alcohol (specific gravity .815), compared with atmospheric air, is 1.613. (GAY-LUSSAC, *Annales de Chim. et Phys.*

tom. i.) According to Berzelius and Dulong, the density of the vapour of anhydrous alcohol is 1.6004. (*Ann. de Chim. et Phys.* xv.) To become vapour, alcohol absorbs only 0.436, the heat required to evaporate an equal weight of water. Dr. Ure, in the *Philos. Trans.*, 1818, has given a table of the forces of vapour of alcohol at different temperatures. The expansibility of alcohol by heat is such, that 1000 parts (specific gravity .817), at 50° , become 1079 parts at 170° . At 110° , half way between the extremes, the alcohol was at 1039, or half a division below the true mean. The more the alcohol is diluted with water, the greater Mr. Dalton found the disproportion to be between the two parts of the scale. When of the specific gravity .967, corresponding to 75 *per cent.* of water, the ratio of expansion through the first half between 50° and 170° , was to that through the second half, as 35 to 45. (*Henry's Elements*, ii. 319; 9th edition.)

Alcohol may be mixed in all proportions, with water, and the specific gravity of the mixture is greater than the mean of the two liquids, in consequence of a diminution of bulk that occurs on mixture, as may be shown by the following experiment:—

The annexed wood-cut represents a tube with two bulbs, communicating with each other, the upper one being supplied with a well-ground glass stopper. Fill the tube and lower bulb with water, pour alcohol slowly into the upper bulb, and when full put in the stopper. The vessel will now be completely filled, the alcohol lying upon the water; if it be inverted, the alcohol and water will slowly mix, and the condensation that ensues will be indicated by the empty space in the tube. A considerable rise of temperature takes place in this experiment, in consequence of the condensation. Thus, equal measures of alcohol (of a specific gravity of .825) and water, each at 50° , afford, when suddenly mixed, a temperature of 70° ; and equal measures of proof spirit and water, each at 50° , give, under similar circumstances, a mixture of the temperature of 60° .

The strength of such spirituous liquors as consist of little else than water and alcohol, is of course ascertained by their specific gravity; and for the purpose of levying duties upon them, this is ascertained by the



hydrometer; an instrument constructed upon the same principle as that described at page 563. But the only correct mode of ascertaining the specific gravity of liquids, is by weighing them in a delicate balance, against an equal volume of pure water, of a similar temperature.

In the *Philosophical Transactions* for 1794, Mr. Gilpin has given a copious and valuable series of tables of the specific gravity of mixtures of alcohol and water, and of the condensation that ensues, with several other particulars. These are extremely useful, as enabling us to ascertain, without difficulty, the relative quantity of alcohol contained in any mixture of known specific gravity.

The original tables are extremely voluminous, and have been variously abridged by different persons; I have, however, thought it most useful to insert two of them, adapted to the temperature of 60°, and refer the reader to Mr. Gilpin's paper for those calculated at other temperatures.

TABLE

OF THE SPECIFIC GRAVITY AND COMPOSITION OF MIXTURES OF ALCOHOL
AND WATER AT THE TEMPERATURE OF 60°.

I. Spirit and Water by Weight. Sp. + W.	II. Specific Gravity.	III. Spirit by Mea- sure.	IV. Water by Measure.	V. Bulk of Mixture.	VI. Diminu- tion of Bulk.	VII. Quantity of Spirit per Cent. by Measure.
100 + 0	.82500	100	—	100.00	—	100.00
1	.82731	—	0.83	100.72	0.11	99.29
2	.82957	—	1.65	101.44	0.21	98.58
3	.83177	—	2.47	102.16	0.31	97.88
4	.83391	—	3.30	102.89	0.41	97.19
100 + 5	.83599	—	4.12	103.62	0.50	96.51
6	.83802	—	4.95	104.35	0.60	95.83
7	.84001	—	5.77	105.09	0.68	95.16
8	.84195	—	6.60	105.83	0.77	94.50
9	.84384	—	7.42	106.57	0.85	93.84
100 + 10	.84568	—	8.25	107.31	0.94	93.19
11	.84748	—	9.07	108.05	1.02	92.55
12	.84924	—	9.90	108.80	1.10	91.99
13	.85096	—	10.72	109.55	1.17	91.28
14	.85265	—	11.55	110.30	1.25	90.66
100 + 15	.85430	—	12.37	111.05	1.32	90.04
16	.85592	—	13.20	111.81	1.39	89.44
17	.85750	—	14.02	112.56	1.46	88.84
18	.85906	—	14.85	113.32	1.53	88.25
19	.86058	—	15.67	114.08	1.59	87.66
100 + 20	.86208	—	16.50	114.84	1.66	87.08
21	.86355	—	17.32	115.60	1.72	86.51
22	.86500	—	18.15	116.36	1.79	85.94
23	.86642	—	18.97	117.12	1.85	85.38
24	.86781	—	19.80	117.88	1.92	84.83
100 + 25	.86918	—	20.62	118.64	1.98	84.28
26	.87052	—	21.45	119.41	2.04	83.74
27	.87183	—	22.27	120.18	2.09	83.21
28	.87314	—	23.10	120.94	2.16	82.68
29	.87442	—	23.92	121.71	2.21	82.16

I. Spirit and Water by Weight.	II. Specific Gravity.	III. Spirit by Mea- sure.	IV. Water by Measure.	V. Bulk of Mixture.	VI. Diminu- tion of Bulk.	VII. Quantity of Spirit per Cent. by Measure.
Sp. + W.						
100 + 30	.87569	100	24.75	122.48	2.27	81.65
31	.87692	—	25.57	123.24	2.33	81.14
32	.87814	—	26.40	124.01	2.39	80.64
33	.87935	—	27.22	124.78	2.44	80.14
34	.88053	—	28.05	125.55	2.50	79.65
100 + 35	.88169	—	28.87	126.32	2.55	79.16
36	.88283	—	29.70	127.09	2.61	78.68
37	.88395	—	30.52	127.86	2.66	78.21
38	.88505	—	31.35	128.64	2.71	77.74
39	.88613	—	32.17	129.41	2.76	77.27
100 + 40	.88720	—	33.00	130.19	2.81	76.81
41	.88825	—	33.82	130.96	2.86	76.36
42	.88929	—	34.65	131.74	2.91	75.91
43	.89032	—	35.47	132.51	2.96	75.47
44	.89133	—	36.30	133.29	3.01	75.03
100 + 45	.89232	—	37.12	134.06	3.06	74.59
46	.89330	—	37.95	134.84	3.11	74.16
47	.89427	—	38.77	135.61	3.16	73.74
48	.89522	—	39.60	136.39	3.21	73.32
49	.89615	—	40.42	137.17	3.25	72.90
100 + 50	.89707	—	41.25	137.95	3.30	72.49
51	.89797	—	42.07	138.73	3.34	72.08
52	.89886	—	42.90	139.51	3.39	71.68
53	.89973	—	43.72	140.29	3.43	71.28
54	.90059	—	44.55	141.07	3.48	70.89
100 + 55	.90144	—	45.38	141.86	3.52	70.49
56	.90227	—	46.20	142.64	3.56	70.11
57	.90309	—	47.02	143.42	3.60	69.72
58	.90391	—	47.85	144.21	3.64	69.34
59	.90470	—	48.67	144.99	3.68	68.97
100 + 60	.90549	—	49.50	145.78	3.72	68.60
61	.90626	—	50.32	146.56	3.76	68.23
62	.90703	—	51.15	147.35	3.80	67.87
63	.90778	—	51.97	148.13	3.84	67.51
64	.90853	—	52.80	148.92	3.88	67.15

I. Spirit and Water by Weight.	II. Specific Gravity.	III. Spirit by Mea- sure.	IV. Water by Measure.	V. Bulk of Mixture.	VI. Diminu- tion of Bulk.	VII. Quantity of Spirit per Cent. by Measure.
Sp. + W.						
100+65	.90927	100	53.62	149.71	3.91	66.80
66	.91001	—	54.45	150.50	3.95	66.45
67	.91074	—	55.27	151.28	3.99	66.10
68	.91146	—	56.10	152.07	4.03	65.76
69	.91217	—	56.92	152.85	4.07	65.42
100+70	.91287	—	57.75	153.64	4.11	65.09
71	.91356	—	58.57	154.42	4.15	64.76
72	.91424	—	59.40	155.21	4.19	64.43
73	.91491	—	60.22	156.00	4.22	64.10
74	.91557	—	61.05	156.79	4.26	63.78
100+75	.91622	—	61.87	157.58	4.29	63.46
76	.91686	—	62.70	158.37	4.33	63.14
77	.91748	—	63.52	159.16	4.36	62.83
78	.91811	—	64.35	159.95	4.40	62.52
79	.91872	—	65.17	160.74	4.43	62.21
100+80	.91933	—	66.00	161.53	4.47	61.91
81	.91933	—	66.82	162.32	4.50	61.61
82	.92052	—	67.65	163.11	4.54	61.31
83	.92110	—	68.47	163.90	4.57	61.01
84	.92168	—	69.30	164.70	4.60	60.72
100+85	.92225	—	70.12	165.49	4.63	60.43
86	.92281	—	70.95	166.29	4.66	60.14
87	.92336	—	71.77	167.08	4.69	59.85
88	.92391	—	72.60	167.87	4.73	59.57
89	.92445	—	73.42	168.66	4.76	59.29
100+90	.92499	—	74.25	169.46	4.79	59.01
91	.92552	—	75.07	170.25	4.82	58.73
92	.92604	—	75.90	171.05	4.85	58.46
93	.92656	—	76.72	171.84	4.88	58.19
94	.92707	—	77.55	172.64	4.91	57.92
100+95	.92758	—	78.37	173.43	4.94	57.66
96	.92807	—	79.20	174.23	4.97	57.40
97	.92856	—	80.02	175.02	5.00	57.14
98	.92905	—	80.85	175.82	5.03	56.88
99	.92954	—	81.68	176.62	5.06	56.62

I. Water and Spirit by Weight.	II. Specific Gravity.	III. Spirit by Mea- sure.	IV. Water by Measure.	V. Bulk of Mixture.	VI. Diminu- tion of Bulk.	VII. Quantity of Spirit per Cent. by Measure.
W. + Sp.						
100+100	.93002	100	82.50	177.41	5.09	56.36
99	.93051	—	83.34	178.22	5.12	56.11
98	.93102	—	84.19	179.05	5.14	55.85
97	.93149	—	85.02	179.89	5.13	55.59
96	.93198	—	85.94	180.74	5.20	55.33
100+95	.93247	—	86.84	181.61	5.23	55.06
94	.93296	—	87.76	182.50	5.26	54.79
93	.93345	—	88.71	183.42	5.29	54.52
92	.93394	—	89.67	184.35	5.32	54.24
91	.93443	—	90.66	185.31	5.35	53.96
100+90	.93493	—	91.67	186.29	5.38	53.68
89	.93544	—	92.70	187.29	5.41	53.39
88	.93595	—	93.75	188.31	5.44	53.10
87	.93646	—	94.83	189.35	5.48	52.81
86	.93697	—	95.93	190.42	5.51	52.51
100+85	.93749	—	97.06	191.53	5.53	52.21
84	.93802	—	98.21	192.65	5.56	51.91
83	.93855	—	99.39	193.80	5.59	51.60
82	.93909	—	100.61	194.99	5.62	51.29
81	.93963	—	101.85	196.20	5.65	50.97
100+80	.94018	—	103.12	197.44	5.68	50.65
79	.94073	—	104.43	198.71	5.72	50.32
78	.94128	—	105.77	200.01	5.76	50.00
77	.94184	—	107.14	201.35	5.79	49.66
76	.94240	—	108.55	202.73	5.82	49.33
100+75	.94296	—	110.00	204.15	5.85	48.98
74	.94352	—	111.48	205.60	5.88	48.64
73	.94408	—	113.01	207.10	5.91	48.29
72	.94465	—	114.58	208.64	5.94	47.93
71	.94522	—	116.20	210.22	5.98	47.57
100+70	.94579	—	117.86	211.84	6.02	47.20
69	.94637	—	119.56	213.51	6.05	46.83
68	.94696	—	121.32	215.24	6.08	46.46
67	.94756	—	123.13	217.02	6.11	46.08
66	.94816	—	125.00	218.85	6.15	45.69

I. Water and Spirit by Weight.	II. Specific Gravity.	III. Spirit by Mea- sure.	IV. Water by Measure.	V. Bulk of Mixture.	VI. Diminu- tion of Bulk.	VII. Quantity of Spirit per Cent. by Measure.
W. + Sp.						
100 + 65	.94876	100	126.92	220.74	6.18	45.30
64	.94936	—	128.90	222.69	6.21	44.91
63	.94997	—	130.95	224.70	6.25	44.50
62	.95058	—	133.06	226.78	6.28	44.10
61	.95110	—	135.25	228.93	6.32	43.68
100 + 60	.95181	—	137.50	231.14	6.36	43.26
59	.95243	—	139.82	233.44	6.38	42.84
58	.95305	—	142.23	235.82	6.41	42.41
57	.95368	—	144.73	238.28	6.45	41.97
56	.95430	—	147.32	240.82	6.50	41.52
100 + 55	.95493	—	150.00	243.47	6.53	41.07
54	.95555	—	152.77	246.22	6.55	40.61
53	.95617	—	155.65	249.08	6.57	40.15
52	.95679	—	158.65	252.05	6.60	39.67
51	.95741	—	161.77	255.14	6.63	39.19
100 + 50	.95804	—	165.00	258.34	6.66	38.71
49	.95867	—	168.37	261.68	6.69	38.21
48	.95931	—	171.87	265.16	6.71	37.71
47	.95995	—	175.53	268.80	6.73	37.20
46	.96058	—	179.35	272.59	6.76	36.68
100 + 45	.96122	—	183.34	276.56	6.78	36.16
44	.96185	—	187.50	280.70	6.80	35.63
43	.96248	—	191.86	285.05	6.81	35.08
42	.96311	—	196.43	289.60	6.88	34.53
41	.96374	—	201.21	294.38	6.88	33.97
100 + 40	.96437	—	206.25	299.42	6.83	33.40
39	.96500	—	211.54	304.71	6.83	32.82
38	.96563	—	217.10	310.28	6.82	32.23
37	.96626	—	222.97	316.15	6.82	31.63
36	.96689	—	229.17	322.36	6.81	31.02
100 + 35	.96752	—	235.71	328.90	6.81	30.40
34	.96816	—	242.65	335.84	6.81	29.78
33	.96880	—	250.00	343.21	6.79	29.14
32	.96944	—	257.81	351.04	6.77	28.49
31	.97009	—	266.13	359.38	6.75	27.83

I. Water and Spirit by Weight. W. + Sp.	II. Specific Gravity.	III. Spirit by Mea- sure.	IV. Water by Measure.	V. Bulk of Mixture.	VI. Diminu- tion of Bulk.	VII. Quantity of Spirit per cent. by Measure.
100 + 30	.97074	100	275.00	368.28	6.72	27.15
29	.97139	—	284.48	377.79	6.69	26.47
28	.97206	—	294.64	387.99	6.65	25.77
27	.97273	—	305.56	398.95	6.61	25.07
26	.97340	—	317.31	410.74	6.57	24.35
100 + 25	.97410	—	330.00	423.48	6.52	23.61
24	.97497	—	343.75	437.29	5.46	22.87
23	.97550	—	358.70	452.31	6.39	22.11
22	.97622	—	375.00	468.64	6.36	21.34
21	.97696	—	392.86	486.58	6.28	20.55
100 + 20	.97771	—	412.50	506.29	6.21	19.75
19	.97848	—	434.21	528.08	6.13	18.94
18	.97926	—	458.33	552.29	6.04	18.11
17	.98006	—	485.29	579.34	5.95	17.26
16	.98090	—	515.62	609.76	5.86	16.40
100 + 15	.98176	—	550.00	644.25	5.75	15.52
14	.98264	—	589.29	683.66	5.63	14.63
13	.98356	—	634.61	729.10	5.51	13.72
12	.98452	—	687.50	782.11	5.39	12.79
11	.98551	—	750.00	844.74	5.26	11.84
100 + 10	.98654	—	825.00	919.87	5.13	10.87
9	.98761	—	916.67	1011.70	4.97	9.88
8	.98872	—	1031.25	1126.44	4.81	8.88
7	.98991	—	1178.57	1273.92	4.65	7.85
6	.99195	—	1375.00	1470.02	4.48	6.80
100 + 5	.99244	—	1650.00	1745.70	4.30	5.73
4	.99380	—	2062.50	2158.37	4.13	4.63
3	.99524	—	2750.00	2846.04	3.96	3.51
2	.99675	—	4125.00	4221.21	3.79	2.37
1	.99834	—	8250.00	8346.38	3.62	1.20

There are other methods of judging of the strength of spirituous liquors, which, though useful, are not accurate, such as the taste, the size and appearance of the bubbles when shaken, the sinking or floating of olive oil in it, and the appearances that it exhibits when burned; if it burns away perfectly to dryness, and inflames gunpowder or a piece of cotton immersed in it, it is considered as *alcohol*. The different spirituous liquors leave variable proportions of water, when thus burned in a graduated vessel. But it must be recollected that in rum, brandy, and several other spirits, the specific gravity is often interfered with by extractive, colouring, and saccharine substances, often fraudulently added with a view to diminish their apparent strength. In examining these liquors, they should be distilled in the manner described above in reference to wine, and the specific gravity of the distilled portion will then give an indication of the proportion of alcohol *per cent.* that may be relied on.

There is some difficulty in ascertaining what is meant by the term *proof spirit*. Dr. Thomson, quoting the Act of Parliament of 1762 (*System*, ii. 319), states, that at the temperature of 60° , the specific gravity of proof spirit should be .916; and he also observes that *proof spirit* usually means a mixture of *equal bulks* of alcohol and water; but the specific gravity of such a mixture will, of course, depend upon that of the standard alcohol, which is not specified. It appears from GILPIN's *Tables*, that spirit of the specific gravity .916, at 60° , consists, *by weight*, of 100 parts of alcohol, specific gravity .825, at 60° , and 75 of water; and, *by measure*, of 100 parts of the same alcohol, and 61.87 of water. From the *Tables* of LOWITZ, quoted by Dr. Thomson, from CRELL's *Annals* (1796, i. 202), we learn, that equal weights of alcohol, specific gravity .796, at 60° , (and which may be regarded as *pure alcohol*,) and water, have a specific gravity of .917, which is very near legal proof, and which, according to GILPIN's *Tables*, contains 62.8 parts *per cent.* of his alcohol, *by measure*. The *proof spirit* of the Pharmacopœia (*spiritus tenuior*) is directed to be of the specific gravity .930.

ALCOHOL is extremely inflammable, and burns with a pale blue flame, scarcely visible in bright day-light. The heat, however, of its flame is very intense, as may be shown by sus-

pending in it a coil of fine platinum wire, which becomes white hot. It occasions no fuliginous deposition upon substances held over it, and the products of its combustion are carbonic acid and water, the weight of the water considerably exceeding that of the alcohol consumed. According to Saussure, jun., 100 parts of alcohol afford, when burned, 186 parts of water, the production of which may be shown by substituting the flame of alcohol for that of hydrogen, in the apparatus described in the first volume, under the Article WATER (vol. i. p. 168), and if the tube at its extremity be turned down into a glass jar, it will be found that a current of carbonic acid passes out of it, which may be rendered evident by lime-water.

There are some substances which communicate colour to the flame of alcohol; from boracic acid it acquires a greenish-yellow tint; nitre and the soluble salts of baryta cause it to burn yellow, and those of strontia give it a beautiful rose colour; cupreous salts impart a fine green tinge.

Alcohol dissolves pure soda and potassa, but it does not act upon their carbonates: consequently, if the latter be mixed with alcohol containing water, the liquor separates into two portions, the upper being alcohol deprived, to a considerable extent, of water, and the lower the aqueous solution of the carbonate, as above stated. The alcoholic solution of caustic potassa was known in old pharmacy, under the name of Van Helmont's *Tincture of Tartar*. Its use in purifying potassa has already been stated (vol. i. p. 389); if the solution be long kept it deposits small crystals of carbonate of potassa, and becomes nearly black, from the decomposition of a portion of alcohol. Ammonia and its carbonates are soluble in alcohol; the greater number of the sulphates are insoluble in this menstruum, but it dissolves many of the muriates and nitrates. It also dissolves the greater number of the acids. It absorbs many gaseous bodies, and generally much more copiously than water. It dissolves the vegetable acids, the volatile oils, the resins, tan, and extractive matter, and many of the soaps; the greater number of the fixed oils are taken up by it in small quantities only, but some dissolve largely. It may be remarked, that many errors exist in the published estimates of the solubility of substances in alcohol, arising from the existence of water either in the solvent or substance dissolved.

Mr. Graham has shown that alcohol may in many instances be combined with saline bodies, performing as it were the part of water of crystallisation. Such combinations may be called *alcoholes*. They are obtained by dissolving the substances by heat in absolute alcohol, and are deposited as the solution cools, more or less regularly crystallised. They appear to be definite compounds, and in some of them the alcohol is retained by an attraction so powerful, as not to be evolved at a temperature of 400 or 500°. Mr. Graham has examined the alcoholic combinations of chloride of calcium, nitrate of magnesia, nitrate of lime, chloride of zinc, and chloride of manganese. (*Quarterly Journal*, N. S., Dec. 1828.)

When the vapour of alcohol is passed through a red-hot copper tube, it is decomposed, a portion of charcoal is deposited, and a large quantity of carburetted hydrogen gas is evolved.

The most satisfactory experiments on the composition of alcohol are those of Saussure, (*Ann. de Chim.*, lxxxix., *Nicholson's Journal*, xxi.) He passed the alcohol through a red-hot porcelain tube, terminating in a glass tube six feet long and surrounded by ice; all the products were carefully collected and weighed. The result of this analysis was, that 100 parts of alcohol, specific gravity 792, at 68°, consist of

Hydrogen	13.70
Carbon	51.98
Oxygen	34.32
						<hr/>
						100

Dr. Ure analyzed alcohol by passing it through ignited peroxide of copper, and the result, corrected to the specific gravity of the alcohol used by Saussure, corroborates the correctness of the latter; he obtained

Hydrogen	14.09
Carbon	49.10
Oxygen	36.81
						<hr/>
						100

Saussure's experiments have also been repeated and verified by Dumas and Boullay. (*Ann. de Chim. et Phys.* 1827.)

These numbers approach to

Three proportionals of hydrogen	.	.	.	=	3
Two „ carbon	.	.	.	=	12
One „ oxygen	.	.	.	=	8
					<hr/>
					23

or we may suppose the elements so arranged as to represent—

One proportional of olefiant gas	.	=	14
„ „ aqueous vapour	.	=	9
			<hr/> 23

Weights which are equivalent to equal volumes, as will be found by dividing them by their densities, for $14 \div .972$, (density of olefiant gas), and $9 \div .625$ (density of aqueous vapour), give very nearly equal quotients, so that alcohol vapour, in reference to the theory of volumes, will be constituted by a volume of olefiant gas, and a volume of aqueous vapour condensed (as may be inferred from the specific gravity of alcoholic vapour) into one volume, thus

Olefiant gas 14	Aqueous vapour 9	=	Vapour of alcohol 23
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The following illustrations of the conversion of sugar into alcohol, I transcribe from the last edition of Dr. Henry's Elements of Chemistry, in which the reader will find a very perspicuous statement of the different views which may be taken of the arrangement of ultimate elements in alcohol and ether.

In order to understand the theory of the production of alcohol, which has been proposed by Gay-Lussac, it is necessary to recapitulate the results of the analysis of sugar, made by that philosopher in conjunction with Thenard. Its composition is as follows:—

Charcoal	42.47
Oxygen and hydrogen in the proportions required to form water	}				57.53

or of 102 volumes of gaseous carbon + 92 volumes of aqueous vapour.

But if we suppose that sugar is composed of 40 parts by weight of charcoal and 60 of water, and convert these weights into volumes, it will then consist of

	1 volume of charcoal in vapour,
or of	1 „ aqueous vapour;
	1 volume of charcoal in vapour,
	1 „ hydrogen,
	$\frac{1}{2}$ „ oxygen.

But alcohol, it has already been stated, is constituted of

$$\begin{aligned} 1 \text{ volume of olefiant gas} &= \begin{cases} 2 \text{ volumes of vapour of charcoal,} \\ 2 & \text{,, hydrogen,} \end{cases} \\ 1 & \text{,, aqueous vapour} = \begin{cases} 1 \text{ volume of hydrogen,} \\ \frac{1}{2} & \text{,, oxygen,} \end{cases} \end{aligned}$$

or

$$\text{Alcohol} \dots\dots\dots = \begin{cases} 2 \text{ volumes of vapour of charcoal,} \\ 3 & \text{,, hydrogen,} \\ \frac{1}{2} & \text{,, oxygen.} \end{cases}$$

And tripling the numbers representing the elements of sugar, in order to equalize the hydrogen of both,

$$\text{Sugar} \dots\dots\dots = \begin{cases} 3 \text{ volumes of vapour of charcoal,} \\ 3 & \text{,, hydrogen,} \\ 3 \text{ half volumes of oxygen.} \end{cases}$$

Comparing, then, the composition of sugar with that of alcohol, it follows that, to transform the former into the latter, we must remove

$$\begin{aligned} &1 \text{ volume of the vapour of charcoal,} \\ &1 & \text{,, oxygen gas,} \end{aligned}$$

which, by combining, form one volume of carbonic acid. Reducing these volumes to weight, 100 pounds of sugar should afford 51.34 of alcohol, and 48.76 of carbonic acid*.

When alcohol is submitted to distillation with certain acids, peculiar compounds are formed, called *ethers*; they are distinguished by the name of the acid employed in their preparation.

SULPHURIC ETHER.

Sulphuric Ether is the most important of these compounds; it is prepared as follows: equal weights alcohol and sulphuric acid are carefully mixed and introduced into a glass retort placed in a sand-bath, to which is adapted a capacious tubulated glass globe, connected with a receiver, as represented in the wood-cut at page 205, vol. i. Raise the mixture in the retort to its boiling point as rapidly as possible, and, keeping the receiver cool by water or ice, continue the distillation, till opaque vapours appear in the retort; then remove the receiver, and agitate its contents with a little quicklime; after which pour off the clear liquor, and redistil to the amount of three-

* Gay-Lussac, *Ann. de Chim.*, xcv. 311.

fourths its original quantity with the same precautions as before. The ether may be further purified by distilling it off muriate of lime. The *London Pharmacopœia* directs the distillation of ether with potassa, for its purification from sulphurous acid; and Mr. Richard Phillips, in his *Experimental Examination*, has given the following directions for procuring ether for pharmaceutical purposes, which answer extremely well. "Mix with 16 ounces of sulphuric acid, an equal weight of rectified spirit, and distil about 10 fluid ounces, add 8 ounces of spirit to the residuum in the retort, and distil about 9 fluid ounces; or continue the operation until the contents of the retort begin to rise or the product becomes considerably sulphurous; mix the two products, and if the mixture consist of a light and heavy fluid, separate them: add potash to the lighter, as long as it appears to be dissolved; separate the ether from the solution of potash, and distil about nine-tenths of it, to be preserved as *ether sulphuricus*, the specific gravity of which ought to be at most .750."

Preparing ether upon a larger scale, it is found that 14 parts of alcohol (specific gravity .820) mixed with an equal weight of sulphuric acid (specific gravity 1.8), and submitted to distillation, afford about 8 parts of impure ether (specific gravity .770). To the residuum 7 parts of alcohol may be added, and about $7\frac{3}{4}$ parts more of impure ether drawn off. These products, when mixed, have a specific gravity of about .782, and when rectified by distillation on carbonate of potassa, afford $10\frac{1}{2}$ parts of ether, of a specific gravity of .735, and about $3\frac{1}{2}$ parts of ethereal spirit, which is employed instead of an equal quantity of alcohol in the next operation. At Apothecaries' Hall, the distillation of ether is carried on in a leaden still, heated by means of high pressure steam carried through it in a contorted leaden pipe. The still has a pewter head, and is connected with a very capacious condensing worm, duly cooled by a current of water; the receivers are of pewter with glass lids, and have a side tube to connect them with the delivering end of the worm-pipe. In conducting this operation too much caution cannot be observed in avoiding the proximity of fire, and the use of fragile vessels. The whole process of etherification has engaged much of the attention of Mr. Hennell, who has communicated two papers connected with it to the Royal Society (printed in the

Phil. Trans. for 1826 and 1828), and has examined it in most of its details. The best temperature for the distillation of ether (from a mixture of equal weights of alcohol, specific gravity .820, and sulphuric acid, of 1.85) is between 220° and 230° . At that temperature the distillation may be continued till the product equals about half that of the original quantity of alcohol. This portion will have a specific gravity of about .760. The steam is now turned off, and the still allowed to cool, when a fresh portion of alcohol is added to its contents, equal to half that originally employed, and the distillation resumed and continued till a quantity equal to the first product is obtained, having a specific gravity from .765 to .770; and now the distillation proceeds very tardily unless the heat be increased, in which case sulphurous acid is evolved; and if what passes over be examined, it will be found to separate into two portions, of which the lighter only is ethereal, and but small in quantity. Mr. Hennell, however, found, that if at this period of the process small portions of water be admitted at short intervals to the contents of the still (which is easily effected by a funnel tube and stop-cock passing to the bottom of the still), the evolution of ether will be, for a time, resumed and increased. The products of the distillations having been mixed together, are agitated with a sufficient quantity of dry carbonate of potassa, and very gently redistilled until about nine-sixteenths have passed over: this is ether as it occurs in commerce, and has a specific gravity of from .730 to .735. To obtain from it *pure* ether, it may be agitated in a well stopped bottle with dry powdered chloride of calcium: the fluid separates into two portions; the heavier is an alcoholic solution of the chloride; and the lighter, poured off and redistilled, yields pure ether.

When ether, obtained by the usual process, is washed with its bulk of water, its specific gravity is diminished, and the water employed for washing it affords, on distillation, a considerable portion of alcohol, which may, of course, be economically preserved. This *washed ether* has some peculiarities in respect to its solvent powers which deserve further investigation.

Sulphuric ether is a transparent, colourless liquid, of a pleasant smell and a pungent taste; it is highly exhilarating,

and produces a degree of intoxication when its vapour is inhaled by the nostrils. Its specific gravity varies extremely with its purity. Lowitz is said to have procured it as light as .632. I have never obtained it lower than .700; and, as ordinarily prepared, its specific gravity varies between .730 and .760. As met with in commerce, it must always be considered as a mixture of pure ether and alcohol. The following table is constructed by Mr. Dalton, from direct experiments, on mixtures of ether, specific gravity .720, with alcohol of specific gravity .830.

Ether.	Alcohol.					Specific Gravity.
100	+	0	.	.	.	0.720
90	+	10	.	.	.	0.732
80	+	20	.	.	.	0.744
70	+	30	.	.	.	0.756
60	+	40	.	.	.	0.768
50	+	50	.	.	.	0.780
40	+	60	.	.	.	0.792
30	+	70	.	.	.	0.804
20	+	80	.	.	.	0.816
10	+	90	.	.	.	0.828
0	+	100	.	.	.	0.830

It appears, from this table, that the rectified ether of the shops, of a specific gravity = .750, contains about 25 *per cent.* by weight of alcohol. (HENRY'S *Elements*, ii. 333.)

Sulphuric ether is extremely volatile, and when poured from one vessel into another, a considerable portion evaporates; during its evaporation from surfaces, it produces intense cold, as may be felt by pouring it upon the hand; and seen, by dropping it upon the bulb of a thermometer, which sinks to many degrees below the freezing point. The specific gravity of the vapour of sulphuric ether, compared with atmospheric air, is, according to Gay-Lussac, as 2.586 to 1.000. Two ounce measures of ether converted into gas at the temperature of 72.50 fill the space of a cubic foot.

At mean pressure, sulphuric ether, when of a specific gravity of .720, boils at 98°, and under the exhausted receiver of the air pump, at all temperatures above -20°; hence, were it not for atmospheric pressure, ether would only be known in the state of vapour.

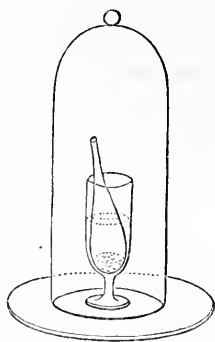
The force of ethereal vapour, at different temperatures, has been examined by Dr. Ure and Mr. Dalton; the latter has

also determined the boiling points of mixtures of ether and alcohol, and has shown that they are nearer that of ether, than the proportions between the alcohol and ether would indicate.

In consequence of the cold produced during the vaporization of sulphuric ether, the phenomena of boiling and freezing may be exhibited in the same vessel. For this purpose, procure a very thin flask which fits loosely into an ale glass, as shown in the margin. Pour a small quantity of ether into the flask, and of water into the glass, and place the whole under the receiver of an air-pump; during exhaustion, the ether will boil, and a crust of ice will gradually form upon the exterior of the flask.

When subjected to a degree of cold equal to -46° , sulphuric ether freezes.

From the experiments of Girard, it appears that ether passes more rapidly through a capillary orifice than water, and water more rapidly than alcohol. The relative times for equal measures of each fluid, at the temperature of 55° , being 101" for ether, 349" for water, and 856" for alcohol. (*Ann. de Chim. et Phys.* vi. 226.)



When ether is kept for a long time in vessels which are occasionally opened and exposed to light, a small portion of vinegar forms in it, and it becomes less volatile, and less capable of dissolving fixed oil; hence it should be preserved in a dark place, and in bottles entirely full. (PLANCHE, *Ann. de Chim. et Phys.* ii. 273.)

Ether dissolves the resins, several of the fixed oils, and nearly all the volatile oils; it also dissolves a portion of sulphur, and of phosphorus; the latter solution is beautifully luminous when poured upon warm water, in a dark room; and both it and the sulphuretted ether deposit crystals when kept for a long time subject to a very slow evaporation. The fixed alkalis are not soluble in ether, but it combines with ammonia.

Ether dissolves the oxides of gold and platinum, and these solutions have been employed for coating steel with those metals, with a view to ornament and as a defence from rust. If to a saturated solution of gold or platinum, in nitro-muriatic acid, there be added about 3 parts by measure of good sulphuric ether, it soon takes up the metals, leaving the acid

nearly colourless below the ethereal solution, which is to be carefully decanted off; into this the polished steel is for an instant plunged, and immediately afterwards washed in water, or in a weak alkaline solution. Though the coating of platinum is the least beautiful, Mr. Stodart, who has made many experiments upon this subject, considers it as the best protection from rust. Polished brass may be coated by the same process. These surfaces of gold and platinum, though very thin, are often a useful protection: with gold the experiment is particularly beautiful, and well illustrates the astonishing divisibility of the metal. The ethereal solution of gold is not permanent, but, after a time, deposits the metal in the form of a film, in which crystals of gold are often perceptible.

Ether is sparingly soluble in water, and in alcohol it dissolves, as above stated, in all proportions. The *spiritus ætheris sulphurici* of the *Pharmacopœia*, is an alcoholic solution of ether.

Ether is highly inflammable, and in consequence of its volatility it is often kindled by the mere approach of a burning body; a circumstance which renders it highly dangerous to decant, or to open vessels of ether near a candle.

The inflammability of ethereal vapour may be shown by passing a small quantity into a receiver, furnished with a brass stop-cock and pipe, and inverted over water at the temperature of 100°. The receiver becomes filled with the vapour, which may be propelled and inflamed: it burns with a bright bluish white flame.

When ether is admitted to any gaseous body it increases its bulk. Oxygen thus expanded, produces a highly inflammable mixture; if the quantity of oxygen be large, and of ether small, the mixture is highly explosive, and produces water and carbonic acid.

When a little ether is introduced into chlorine, the gas is absorbed, and a peculiar compound results, in which muriatic acid is very perceptible; if the ether be inflamed, a large quantity of charcoal is deposited, and muriatic acid gas is abundantly evolved. When a small quantity of ether is poured into a large jar of warm chlorine, it occasionally happens that a considerable explosion ensues.

When ether is passed over red-hot platinum wire, or con-

sumed in the lamp without flame, described in the Chapter on Radiant Matter (vol. i. p. 130), a peculiar acid substance is produced, which has been subjected to an interesting series of experiments, by Mr. J. F. Daniell, (*Quarterly Journal of Science and Arts*, vi. 318.) He obtained it by placing the lamp, filled with ether, and properly trimmed with a coil of glowing platinum wire, under the head of an alembic, in which the vapour was condensed, and collected in a phial applied to its beak.

Lampic acid, for so Mr. Daniell has termed this product, is colourless, sour, and pungent; its vapour is very irritating, and its specific gravity, when purified by carefully driving off a portion of alcohol which it contains, is about 1.015. It redens vegetable blues, and decomposes the alkaline carbonates with effervescence.

Mr. Daniell has described many of the combinations of this acid, which he terms *lampates*, and has given some experiments upon its composition.

When lampic acid is added to the solutions of silver, gold, platinum, mercury, and copper, and the mixture heated, the metals are thrown down in the metallic state.

On distilling the *lampate of mercury*, made by digesting the peroxide of mercury in the acid, Mr. Daniell obtained the concentrated or pure lampic acid, in the form of a very dense liquid with an intensely suffocating odour.

Such are the properties which at first induced Mr. Daniell to consider the above product as a peculiar acid, but, upon further inquiry into its nature and combinations (*Quarterly Journal*, xii. 64), he found the acid to be the acetic, combined with some compound of carbon and hydrogen, differing from alcohol and from ether, and conferring upon it those properties, in respect to certain metallic solutions, which have been just mentioned. It seems not improbable that some formic acid may also be formed in the process.

The ultimate composition of sulphuric ether (specific gravity 715 at 68°) was determined by Saussure as follows:—

Carbon	67.98
Hydrogen	14.40
Oxygen	17.62
					<hr/>
					100

Or, *per cent.*,

Carbon	64.9
Oxygen	21.6
Hydrogen	13.5
							<hr/> 100

Comparing the composition of alcohol, therefore, with that of sulphuric ether, it would appear that the former is converted into the latter by the abstraction of one half of what may be called its elementary water; for the vapour of alcohol consists of *equal volumes* of olefiant gas and aqueous vapour, condensed into one half of their united bulk, or of one proportional of olefiant gas = 14, and one of water = 9; whereas the vapour of ether consists of *two* volumes of the former, and *one* of the latter, condensed into one volume, or *two* proportionals of olefiant gas (14×2) = 28, and *one* of water = 9, as shewn in the following comparative diagrams:—

23 parts of alcohol (by weight) consist of

One proportional of olefiant gas = 14.	One proportional of aqueous vapour = 9.
--	---

$$14 + 9 = 23$$

Resulting
volume of
alcoholic
vapour.

37 parts of ether (by weight) consist of

Two proportionals of olefiant gas	One proportional of aqueous vapour = 9.
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$$14 \times 2 = 28.$$

$$28 + 9 = 37$$

Resulting
volume of
ethereal
vapour.

Theory of Etherification, production of Sulphovinic Acid, and Oil of Wine.—From the above statement, it has been inferred, that the whole operation of the sulphuric acid in converting alcohol into ether, consisted in its power of abstracting water, or the elements of water; but the experiments of Ser-tuerner, Vogel, and others, shewed that the acid underwent more complicated changes; and these have lately been ably investigated by Mr. Hennell, in the memoirs already quoted.

Sertuerner found the sulphuric acid considerably changed in its properties; and called the new acid, which he conceived to result from these changes, *Ænothionic acid*. Vogel afterwards found, that by the action of the alcohol, the sulphuric acid lost much of its power of precipitating the soluble salts of lead; and he called the acid into which it was converted, *Sulphovinic acid*, which term we still retain. Mr. Hennell's experiments shew, that the mutual action of the sulphuric acid and alcohol is immediate upon mixture; that its saturating power is diminished; that the new acid forms soluble salts with baryta and oxide of lead; that it is constituted by the union of sulphuric acid with part of the hydrocarbon of the alcohol; and that it forms peculiar salts with bases. When the mixture of alcohol and sulphuric acid, containing this sulphovinic acid, is distilled, ether is, as we have seen, the principal product; and during the formation of the ether, the sulphovinic acid gradually returns to the state of sulphuric acid, imparting its hydrocarbon to the water, or elements of water present, under such circumstances, and in such proportions as to form ether. If, however, instead of immediately proceeding to distillation, the mixture of sulphuric acid and alcohol be diluted, the sulphovinic acid remains entire; but, upon distilling the diluted mixture, it disappears as before; but now, instead of generating ether, alcohol is *produced* by the union of the hydrocarbon which the sulphovinic acid throws off, with a double proportion of water. These are the most important points of Mr. Hennell's results; and the conclusions which he has drawn appear to be sanctioned and verified by the following experiments.

The immediate change in the sulphuric acid is rendered evident by the following experiments:—440 grains of sulphuric acid were mixed with an equal weight of alcohol, specific gravity .820; the mixture, when cold, was diluted with water, and saturated by carbonate of soda, of which it required only 398 grains; whereas 440 grains of sulphuric acid saturated 555 grains of the same carbonate: here, therefore, two-sevenths of the acid seem to have been saturated by, or to have entered into some new combination with the alcohol.

440 grains of sulphuric acid were mixed, as before, with its weight of alcohol, and the mixture poured into a solution of

acetate of lead ; 542 grains of sulphate of lead only were precipitated ; whereas the same quantity of sulphuric acid not acted upon by alcohol, threw down 1313 grains of sulphate of lead, so that four-sevenths of the acid had lost its power of precipitating oxide of lead.

Vogel and Gay-Lussac have attributed this loss of saturating power to the formation of hyposulphuric acid ; and they regard the hyposulphates and sulphovinates as only differing in the latter containing ethereal oil, which in some way acts the part of water of crystallization. But that this is not a correct view of the phenomena, will appear from the following experiments on the nature of oil of wine, and of sulphovinic acid.

Oil of Wine.—When the distillation of a mixture of sulphuric acid and alcohol is carried beyond the point at which ether ceases to come over, a portion of a liquid, looking like oil, is obtained ; which, when washed, has a bitter aromatic flavour, and has long been known under the name of *oil of wine*, and generally regarded as analogous in composition to the volatile oils. In endeavouring to determine the ultimate elements of this oil, by passing it over red-hot oxide of copper, Mr. Hennell always obtained sulphurous acid, and a solution of sulphate of copper on washing the oxide he had used, notwithstanding that every precaution had been taken to free the oil of wine from all adhering acid. A few drops of the oil were added to a solution of muriate of baryta, and gently heated, but no cloud was produced, although litmus paper indicated the presence of free acid ; when evaporating the mixture, however, a precipitate fell as it became concentrated ; and, on boiling to dryness, sulphate of baryta was found in the residue. It appeared, therefore, that the sulphuric acid was in some state of combination which prevented its usual action upon tests ; or that its elements were in some peculiar state of arrangement in the oil of wine. Mr. Hennell made some experiments to determine the quantity of sulphuric acid thus elicited, from which it appeared, that 100 grains of the oil of wine afforded about 38 grains of sulphuric acid. His previous experiments had shown him that hydrogen and carbon were also elements of oil of wine ; and, having determined their proportions by

distillation through oxide of copper (adhering moisture and acid having been removed from the oil of wine by quicklime), he obtained, from 100 grains (mean of several experiments),

Hydrogen	8.30
Carbon	53.70
							<hr/>
							62

which appeared to indicate the composition of oil of wine to be 62 hydrocarbon, 38 sulphuric acid. It will be observed, that, as respects the carbon and hydrogen, the relative proportions nearly approximate to 6 and 1. Mr. Hennell observes, however, in regard to the above experiments, that we can only infer from them the composition of the hydrocarbon combined with and neutralizing the sulphuric acid; for that oil of wine dissolves a variable quantity of hydrocarbon, part of which separates in a crystalline form when the oil is kept for some time, or when exposed to cold. Having thus far determined the composition of oil of wine, its action upon heated solutions of muriate of baryta, and of potassa, was more particularly examined; it having been already observed, that in those cases an acid is evolved which does not precipitate baryta. Two hundred grains of oil of wine were gently heated with 6 ounces of water for an hour; precipitated carbonate of baryta was then added, which dissolved, with effervescence, to the amount of 90 grains: the solution, filtered and set to evaporate, became acid, and deposited sulphate of baryta. The experiment, therefore, was repeated; but instead of evaporating the barytic solution, it was precipitated by carbonate of potassa, and filtered. The filtered solution evaporated at a temperature not exceeding 150° , remained neutral, and afforded lamellar crystals, greasy to the touch, very soluble in water and alcohol, burning, when heated, with a flame like that of ether, and leaving an acid sulphate of potassa. To determine the composition of the crystals, 20 grains were heated to redness, and left a residue of 10.56 grains of sulphate of potassa, equal to 4.8 sulphuric acid, and 5.76 potassa. 20 grains were dissolved in a solution of caustic potassa, boiled to dryness, heated red-hot, and, when cold, dissolved in distilled water; the excess of potassa was then saturated by nitric acid, and the solution added to one of muriate of baryta: 28 grains of sulphate of

baryta were obtained, nearly equal to 9.6 of sulphuric acid : the salt, therefore, contained twice the quantity of sulphuric acid required to form a neutral salt with the potassa, or *two proportionals*. The remaining elements of the salt were determined by heating it with oxide of copper, from which it appeared that the components of 100 grains are,

Potassa	28.84
Sulphuric acid	48.84
Carbon	13.98
Hydrogen	2.34
Water	7.

These numbers may be considered as indicating

1	proportional of potassa	.	.	=	48
2	„ sulphuric acid	.	.	=	80
4	„ carbon	.	.	=	24
4	„ hydrogen	.	.	=	4
					<hr/>
					156

Mr. Hennell proceeds to shew that the salts obtained from oil of wine are identical with the sulphovinates procured from the mixture of sulphuric acid and alcohol; the sulphovinic acid, therefore, must be regarded as a compound of two proportionals of sulphuric acid, and one of hydrocarbon, (consisting of 4 proportionals of carbon = 24, and 4 hydrogen = 4;) and corresponding, therefore, to the quadrihydrocarbon above described. (Vol. i. p. 331.) This acid, however, has the property of neutralizing single proportionals only of bases, so that one proportional of the sulphuric acid appears to be neutralized by the hydrocarbon, furnishing an analogous instance to the sulphonaphthalic acid already mentioned. (Vol. i. p. 334.)

When sulphovinates are formed through the medium of oil of wine, a portion of quadrihydrocarbon is thrown off, amounting to half that which is contained in the oil; now, as oil of wine is a perfectly neutral compound, it may, in fact, be regarded as a sulphovinate of hydrocarbon, which in it performs the part of a base; it is composed of

2	proportionals of sulphuric acid	(40 × 2)	=	80
2	„ quadrihydrocarbon	(28 × 2)	=	56
				<hr/>
Equivalent of oil of wine				136

When heated with certain bases, as above described, it throws

off one proportional of quadrihydrocarbon, and becomes sulphovinic acid, constituted by

2	proportionals of sulphuric acid	(40 × 2)	=	80
1	„ quadrihydrocarbon	.	=	28
				<hr/>
	Equivalent of sulphovinic acid	.	.	= 104

Having thus shewn the nature of oil of wine*, of sulphovinic acid, and of the sulphovimates, Mr. Hennell next directed his attention to the part which the sulphovinic acid performs in the generation of ether.

It has already been stated, that when alcohol and sulphuric acid, in equal weights, are put together without the application of any heat beyond that generated during the mixture, the most abundant and important product is sulphovinic acid, above one half of the sulphuric acid being almost immediately converted into that peculiar acid by union with hydrocarbon. But when such a mixture containing so large a proportion of sulphovinic acid is distilled, the most important product is a new substance, namely, ether, and the sulphovinic acid disappears. The questions which then arose were, whether the *ether* was formed altogether from the direct action of the remaining alcohol and sulphuric acid in the mixture; or whether the sulphovinic acid might not also assist; or whether it might not be an essential state of the elements intermediate between the mixture of the acid and alcohol and the development of the perfectly formed ether. MM. Dumas and Boullay, who have considered the same questions, or at least some of them, decide, that the portions of materials which form ether are altogether independent of those which produce sulphovinic acid: but the following facts are urged by Mr. Hennell as contrary to such conclusion.

A portion of oil of vitriol was selected for some comparative experiments, and also some alcohol of specific gravity 0.820 : 500 grains of the oil of vitriol precipitated by acetate of lead, gave 1500 grains of sulphate of lead.

500 grains of the oil of vitriol were mixed with 500 grains of the alcohol, and after forty-eight hours, diluted and precipi-

* I do not here advert to the experiments of Messrs. Dumas and Boullay, because it is evident, that, instead of experimenting upon oil of wine, they used, under that name, the hydrocarbon separable from it.

tated by acetate of lead; only 616 grains of sulphate of lead were produced: so that very nearly three-fifths of the sulphuric acid had become sulphovinic acid by the effect of mixture, and little more than two-fifths remained to act as sulphuric acid upon the remaining alcohol,—full two-thirds of the quantity employed.

Another mixture of acid and alcohol in the same proportions, and made at the same time, was then distilled until 117 grains had passed over, consisting of water, alcohol, and a portion of ether. The residue had not undergone any charring; and being diluted, was precipitated by the acetate of lead: the quantity of sulphate of lead obtained, amounted to 804 grains, *indicating an increase in the quantity of sulphuric acid equivalent to 188 grains of sulphate of lead.*

A similar mixture of alcohol and sulphuric acid, made at the same time and in the same proportions as the two former, was then distilled until 200 grains had been received, the greater part of which was ether; the uncharred residual matter in the retort being then diluted, was precipitated by acetate of lead as before; 986 grains of sulphate of lead were obtained. This contained nearly two-thirds of the sulphuric acid first added, and the increase by distillation had been much more than one-half of that which existed before the application of heat: *so that during the distillation, and simultaneously with the formation of ether, a quantity of sulphovinic acid had been reconverted into sulphuric acid, and the latter appeared to increase in quantity in proportion to the increase of ether in the distilled products.*

A similar mixture of alcohol and acid, made at the same time and in the same proportions as the three former, was then distilled until 200 grains had passed over. 200 grains of water were added to the contents of the retort; 160 grains were distilled off; a second addition of 200 grains of water was made, and the distillation continued; a further addition of 500 grains of water was made, and the operation continued, until as much product had been separated as equalled the water added;—the object was to separate all the ether and alcohol possible, for the purpose of ascertaining to what extent the conversion of sulphovinic acid into sulphuric could be carried. No smell of sulphurous acid was produced during

the operation, nor did any charring of the contents of the retort occur; when precipitated by acetate of lead, 1480 grains of sulphate of lead were obtained. This is very little short of the 1500 given by the acid when unacted upon by alcohol, and shows that *nearly the whole of the sulphovinic acid had been changed back into the state of sulphuric acid*; and is completely at variance with the opinion, that when sulphuric acid and alcohol act upon each other, hyposulphuric acid is formed.

From these experiments it appeared probable that the ether was the product of the decomposition of the sulphovinic acid: but a mixture of equal weights of alcohol and sulphuric acid contains, besides the sulphovinic acid, a considerable quantity of unaltered acid and alcohol; for in such a mixture three-fifths of the sulphuric acid would be converted into sulphovinic acid by combination with the hydrocarbon of less than one-third of the alcohol employed. Mr. Hennell, therefore, next proceeded to ascertain, whether, when no alcohol was present, ether would be produced by the decomposition of sulphovinic acid. A quantity of the sulphovinate of potassa was therefore prepared, the composition of which has been given above, and of which one hundred parts contain 28.84 of potash. 500 grains were mixed with 150 grains of sulphuric acid, being nearly the equivalent of the potash in the salt, and then heat applied. The experiment, therefore, may be considered as the distillation of sulphovinic acid mixed with sulphate of potash, which it may be presumed remained inert during the process, and also with the water of the acid and of the salt. The proportion of water, it is found, has an important influence; but in the present experiment about a drachm of fluid distilled over, and left a blackened and acid salt in the retort, having the smell of sulphurous acid. A few grains of carbonate of potassa being added to the distilled product, abstracted a little water: the clear decanted liquor was then mixed with a little dry muriate of lime, and by agitation separated into two portions; the upper one being decanted, amounted to nearly half a drachm, and was found to be pure ether. *This result proves that ether may be formed from a sulphovinate or sulphovinic acid when no alcohol is present.*

An experiment similar to the last in the nature and proportions of the substances used, was made, except that the sulpho-

vinate was dissolved in its own weight of water previous to the addition of the sulphuric acid. The experiment is one, therefore, of the distillation of dilute sulphovinic acid, in place of that which is concentrated. The distilled product had no smell of ether, nor could any be discovered in it. About nine fluid drachms were obtained; to these, carbonate of potassa was added, which separated the water, and left three drachms of a supernatant liquid, appearing by taste, smell and flame, to be alcohol: this was decanted, and poured upon muriate of lime; no ether separated, but the whole formed one solution; being distilled from the muriate it was evidently alcohol; and being mixed with its weight of sulphuric acid, gave sulphuric ether or sulphovinic acid again. *Alcohol therefore may be formed by the decomposition of sulphovinic acid, when a sufficiency of water is present.*

In this experiment there was no charring of the contents of the retort; and by precipitation by acetate of lead, the whole of the sulphuric acid was obtained;—not only the portion added to decompose the salt, but the double portion evolved from the sulphovinic acid upon the separation and re-arrangement of the hydrocarbon.

It appears, therefore, that in the usual process for obtaining ether, the ether is not formed altogether from the direct action of the alcohol and sulphuric acid considered independently of the sulphovinic acid present, but that the formation of sulphovinic acid is a necessary and intermediate step to the production of ether from alcohol and sulphuric acid. In reference to this subject Mr. Hennell has observed that, in no manner which has yet been devised can ether be formed from alcohol and sulphuric acid without the presence of sulphovinic acid. Whenever ether has been formed, sulphovinic acid has been present; whenever the sulphuric acid is diluted so far as not to form sulphovinic acid with alcohol, it also refuses to form ether with alcohol. Sulphovinic acid will produce ether without the assistance of alcohol. And although the ether produced when a mixture of equal weights of alcohol and sulphuric acid are distilled, appears to be in greater quantity than can arise from the decomposition of the sulphovinic acid existing in the mixture previous to the action of heat, it is not inconsistent to suppose, that at the same time that one portion of sulpho-

vinic acid is resolved into sulphuric acid and ether, another may be formed from alcohol and sulphuric acid.

It has been stated, that the production of ether is materially influenced by the quantity of water present, and that the same sulphovinic acid will yield either ether or alcohol, as it is in a concentrated or dilute state. The hydrocarbon, which has the extraordinary power in oil of wine of neutralizing the whole of the acid properties of sulphuric acid, and in sulphovinic acid of neutralizing the half of them, being in the latter body in so peculiar a condition that it will unite either with that proportion of water necessary to form ether, or with the larger proportion requisite to form alcohol, according to circumstances.

When ether and sulphuric acid are heated together, oil of wine and sulphovinic acid are amongst the products obtained; and as this sulphovinic acid is readily converted when diluted into alcohol and sulphuric acid, so it affords a method of converting ether into alcohol: thus ether may be formed from alcohol, and alcohol from ether at pleasure, by throwing the hydrocarbon of these bodies into that peculiar state which it assumes when combined with sulphuric acid in sulphovinic acid. We may even proceed beyond this, and form either alcohol or ether, using olefiant gas as the hydrocarbon base: for olefiant gas by combining with sulphuric acid, forms sulphovinic acid, and the acid so produced forms either ether or alcohol, according to circumstances which are under perfect command.

NITRIC ETHER.

When strong nitric acid and alcohol are mixed in equal proportions, a violent action presently ensues; there is a very copious evolution of an inflammable æriform body, which has been called *nitrous etherized gas*, and which appears to be a compound of nitrous ether, and nitric oxide. If we endeavour to condense the volatile products, we find that the receiver contains alcohol, water, nitrous ether, nitrous acid, and acetic acid; and that the greater portion of the true ether has made its escape with the gaseous products. Thenard has paid much attention to this subject, and has given the following process

for obtaining nitric ether (*Mémoires d'Arcueil*, tom. i., and *Traité de Chimie*, tom. iii. p. 278) :—

Introduce into a sufficiently capacious tubulated retort equal weights of alcohol (specific gravity .820) and of nitric acid of commerce (specific gravity 1.30), and connect it with five Wolfe's bottles, the first of which is empty, and the remaining four half-filled with a saturated solution of common salt in water. Apply a gentle heat to the retort, till the liquor begins to effervesce; then withdraw the fire, and the gaseous matter passing through the bottles, which should be kept cold by ice, deposits the ether upon the saline solution, from which it is to be decanted, shaken with chalk, and redistilled at a very gentle heat. In performing this experiment, the retort should not be more than one-sixth filled with the mixture of acid and alcohol, and means should be at hand to cool it, if required, in order to subdue the violence of the effervescence. The alcohol should be first poured in, and then the acid, and not mixed by agitation. If the materials are warm, the acid fuming, and the alcohol of proper strength, the action often begins immediately upon mixture, with a cracking noise, escape of air bubbles, and great effervescence, so that the materials, notwithstanding the size of the retort, are very apt to boil over into the first receiver; this may often be prevented by applying a wet cloth to the retort. The tubes through which the vapour is to pass should not be too small, for, in consequence of the suddenness and abundance of its extrication, it requires a ready means of escape.

Nitric ether, thus prepared, has the following properties: It has a very powerful ethereal odour: its colour is pale yellow; its taste very pungent; its specific gravity above that of alcohol, but less than that of water,—according to Dumas, .886 at 40°. It is more volatile than sulphuric ether, and the heat of the hand is sufficient to produce its ebullition. I have frequently observed it boil upon taking the stopper out of the phial. It is slightly acid, and reddens litmus. It is soluble in 48 parts of water; and in all proportions in alcohol; this last solution is the *spiritus ætheris nitrici*, or *sweet spirit of nitre*, of the *Pharmacopæia*. It is decomposed by keeping, and nitric and acetic acids are formed in it; indeed, in the course of a few days its properties begin to change: it becomes

acid, and less volatile. It is very combustible. The specific gravity of its vapour is 2.628.

Nitric ether has been analyzed by Thenard, and by Dumas and Boullay, with the following results:—

	Thenard.	Dumas and Boullay.
Oxygen . . .	48.52	41.46
Carbon . . .	28.45	32.69
Nitrogen . . .	14.49	19.00
Hydrogen . . .	8.54	6.85
	<hr/> 100	<hr/> 100

The numbers in the second column are equivalent to

2	volumes of oxygen.
4	„ carbon.
1	„ nitrogen.
5	„ hydrogen.

Connected with this subject is the production of fulminating mercury and fulminating silver.—See pp. 174 and 189.

Nitric ether, submitted to slow combustion without flame, in the manner above described (p. 588), produces an acrid yellow substance, to which Mr. Daniell has applied the term *Hydrocarburet of Nitrogen*, it appearing from his analysis to consist of 4 proportionals of carbon, 1 of nitrogen, and 11 of hydrogen. (*Quarterly Journal*, xii. 73.)

MURIATIC ETHER.

Muriatic ether [was thus obtained by Thenard (*Mémoires d'Arcueil*, tom. i.): equal measures of strong liquid muriatic acid and highly rectified alcohol, are put into a retort communicating with a receiver, from which a tube passes into a Wolfe's bottle containing warm water, and having a tube of safety: from this there issues a bent tube passing into a bottle surrounded by ice. On applying heat to the retort, a portion of alcohol and acid pass into the first receiver, and the ether in a gaseous state escapes through the warm water and the bent tube, and is condensed in the cold vessel.

At a temperature somewhat below 70° muriatic ether passes into the state of vapour, of which the specific gravity is about 2.220, that of air being 1.000; it is highly inflammable, its

taste sweetish and ethereal, and it is soluble in its own bulk of water at 64° . Its specific gravity in a liquid state, at 40° , is .870. It is remarkable that this ether does not affect vegetable blues, nor does it afford traces of chlorine to the usual tests; but, when burned, muriatic acid is immediately perceptible.

According to Thenard, this ether contains—

Muriatic acid	29.44
Carbon	36.61
Oxygen	23.31
Hydrogen	10.64
					<hr/>
					100

Dr. Thomson considers muriatic ether as a compound of four proportionals of olefiant gas, and one of muriatic acid. Robiquet and Colin resolved it by a red heat into a mixture of 36.79 muriatic acid and 63.21 olefiant gas; and Ampere has shewn that the specific gravity of the vapour of muriatic ether is the same as that of muriatic acid gas + the density of olefiant gas, so that it probably consists of equal volumes of those gases combined without condensation.

Hydriodic Ether.—By distilling two measures of alcohol, with one of concentrated liquid hydriodic acid, Gay-Lussac obtained an ethereal liquid, of a specific gravity of 1.920 at 62° , and requiring a temperature of 148° for its ebullition. Its properties have not been very satisfactorily investigated, nor have any accurate experiments demonstrated its composition. (*Annales de Chimie*, xci.) It is not very inflammable, and becomes coloured by keeping.

Fluoric Ether.—A liquid under this name has been obtained by distilling in a leaden retort a mixture of equal parts of powdered fluor spar, alcohol, and sulphuric acid, but it has not been accurately examined. (NICHOLSON'S *Journ.*, viii. 143.)

Action of Fluoboric Gas on Alcohol.—According to the experiments of M. Desfosses, it appears, that when fluoboric gas is passed into alcohol, a portion of ether analogous to the sulphuric is formed, the liquor becoming at the same time very acid; he refers this change to the attraction of the fluoboric gas for water, which is thus withdrawn from the alcohol, leaving the remaining constituents in the same proportions as in sulphuric ether.

Acetic Ether may be obtained as follows:—Take 100 parts of alcohol, 63 parts of concentrated acetic acid, 17 of sulphuric acid, introduce them into a retort, connected with a large receiver, and distil over about 123 parts. To render it pure, place it, for half an hour, in contact with 10 or 12 parts of caustic potassa, and agitate from time to time. Two strata will form; the undermost, composed of potassa and acetate of potassa dissolved in water; the uppermost, consisting of ether, which may be separated by a long-necked funnel. Sulphuric acid does not enter into the composition of this ether; it merely favours the reaction of the alcohol and acetic acid. We may also obtain acetic ether by taking 3 parts of acetate of potassa, 3 of alcohol, and 2 of sulphuric acid; introducing the mixture into a retort, and distilling to dryness; then mixing the product with the fifth part of its weight of sulphuric acid, and, by a careful re-distillation, drawing off as much ether as there was alcohol employed.

Acetic ether is a colourless liquid, having an agreeable and peculiar odour. It does not redden litmus. Its taste is aromatic. Its specific gravity is 0.866, at 45° F. It boils at 160°. A lighted taper brought near its surface sets fire to it, and it burns with a yellowish-white flame. Acetic acid is developed in the combustion. It is not much changed by keeping. Water, at 62°, dissolves a $7\frac{1}{2}$ part of its weight. When thus dissolved in water, it exercises no action on litmus, and it preserves its characteristic odour and taste. But when this solution is put in contact with half its weight of caustic potassa, its odour and taste disappear, and it is completely decomposed. Hence, if we submit this liquid to distillation, alcohol passes over, and acetate of potassa remains. Acetic ether is very soluble in alcohol. It is sometimes used in medicine as a stimulant.

Ethers from Oxalic Acid, Benzoic Acid, Citric Acid, &c.—When we make a solution of 30 parts of oxalic acid in 35 parts of alcohol, and having added 10 parts of sulphuric acid, subject the whole to distillation till a little sulphuric ether begins to be formed, we shall find that nothing but alcohol slightly etherized has passed into the receiver, and there remains in the retort a brown acid liquor, from which, on cooling, crystals of oxalic acid fall. But when we dilute the residual liquor, a matter is

separated scarcely soluble in water. It is purified by washing it with water, and removing, by a little alkali, the excess of acid which it retains.

If we treat, in the same way, the citric and malic acids, we obtain somewhat similar products; but they differ in taste. That from oxalic acid is astringent and acid; that from the citric acid is bitter. When heated with a solution of caustic potassa, they are all decomposed, and yield alcohol, along with their peculiar acids; but no trace of sulphuric acid.

Tartaric Ether may be obtained from 30 parts of tartaric acid, 35 of alcohol, 10 of sulphuric acid; distil the mixture till a little sulphuric ether begins to be formed. If at this period we withdraw the heat, the liquor assumes a syrupy consistence; but water does not separate the compound of the vegetable acid and alcohol. By adding, by degrees, solution of potassa, we throw down cream of tartar; then, after having just saturated the redundant acid, if we evaporate the liquid, and treat it in the cold with very pure alcohol, we obtain, by evaporation of the alcoholic solution, a substance which, on cooling, becomes syrup. This substance has a brown colour, and a bitter and nauseous taste. It is void of smell and acidity, and is soluble in water and alcohol. It does not precipitate muriate of lime, but copiously the muriate of baryta. When heated it diffuses dense fumes, which have the odour of garlic, and at the same time it leaves a residue, not alkaline, containing much sulphate of potassa. If distilled with potassa, it is resolved into a very strong alcohol, and much tartrate of potassa. It is, therefore, a combination analogous to the preceding. (*See a Memoir of Dumas and Boullay, Ann. de Chim. et Phys.*, January, 1828.)

These ethereal compounds appear generally to consist of peculiar combinations of the vegetable acids with hydro-carbon, and they fully deserve more minute investigation than they have hitherto received. The compound with oxalic acid is peculiarly interesting, in consequence of the singular constitution of that acid.

ACETOUS FERMENTATION.

When any of the vinous liquors are exposed to the free access of atmospheric air, at a temperature of 80° or 85° , they undergo a second fermentation, terminating in the production of a sour liquid, called *vinegar*. During this process a portion of the oxygen of the air is converted into carbonic acid; hence, unlike vinous fermentation, the contact of the atmosphere is necessary, and the most obvious phenomenon is the removal of carbon from the beer or wine; the vinegar of this country is usually obtained from malt liquor, while wine is employed as its source in those countries where the grape is abundantly cultivated.

The colour of vinegar varies according to the materials from which it has been obtained; that manufactured in England is generally artificially coloured with burnt sugar: its taste and smell are agreeably acid. Its specific gravity is liable to much variation; it seldom exceeds 1.0250. When exposed to the air it becomes mouldy and putrid, chiefly in consequence of the mucilage which it contains, and from which it may be in some measure purified by careful distillation. According to Mr. R. Phillips (*Remarks on the London Pharmacopæia*), when good malt vinegar of the specific gravity of 1.020 is distilled, the first eighth that passes over is of the specific gravity 0.997; the next six-eighths are of specific gravity 1.0023, and a fluid ounce decomposes 8.12 grains of precipitated carbonate of lime. The lightness of the first portion is owing to its containing alcohol, consequently, in the *Pharmacopæia* process it is ordered to be rejected. The term *distilled vinegar*, or *dilute acetic acid*, is properly applied to the second portion; it is erroneously called *acetic acid* in the *Pharmacopæia*. The matter which remains in the still is empyreumatic, and generally contains some other vegetable acids: when the vinegar has been adulterated, which is not unfrequently the case, we sometimes find in it muriatic and sulphuric acids.

Distilled vinegar is colourless, and of a flat acid taste; it consists essentially of the real acid diluted with water. To obtain *acetic acid*, or, as it has been sometimes called, *radical vinegar*, distilled vinegar may be saturated with some metallic

oxide, and the acetate thus obtained, subsequently decomposed.

Acetic acid is thus procured by distilling *acetate of copper*, or *crystallized verdigris*, in a glass retort, heated gradually to redness: it requires redistillation to free it from a little oxide of copper which passes over in the first instance. Acetic acid may also be obtained by distilling *acetate of soda* or *acetate of lead* with half its weight of sulphuric acid: or from a mixture of equal parts of sulphate of copper and acetate of lead; in these cases, the acid passes over at a moderate temperature.

A considerable quantity of acetic acid is also now procured by the distillation of wood in the process of preparing charcoal for the manufacture of gunpowder. The liquor at first procured is usually termed *pyroligneous acid*; it is empyreumatic and impure, and several processes have been contrived to free it from tar and other matters which it contains. It may be saturated with chalk, and evaporated, by which an impure acetate of lime will be obtained; and which, mixed with sulphate of soda, furnishes, by double decomposition, sulphate of lime and acetate of soda: the latter, distilled with sulphuric acid, affords a sufficiently pure acetic acid, which, by dilution with water, may be reduced to any required strength; and it may be used generally as a substitute for vinegar: among its other applications, that of preserving animal substances from putrefaction seems important.—(*Quarterly Journal*, x. 173.)

Acetic acid, obtained by these processes, is transparent and colourless, its odour highly pungent, and it blisters and exoriates when applied to the skin. It is extremely volatile, and its vapour readily burns. It combines in all proportions with water, and when considerably diluted, resembles distilled vinegar. When highly concentrated, specific gravity about 1.060, it crystallizes at the temperature of 40° , but liquefies when its heat is a little above that point. In this state it is called *glacial acetic acid*, and consists of one proportional of real acid and one of water ($50 + 9 = 59$). The specific gravity of acetic acid cannot be referred to as a criterion of its strength; for, by the test of its saturating power, it is often found that samples of the same density contain very different proportions of real acid: this arises from the occasional presence of pyroacetic spirit. It is therefore necessary to determine the satu-

rating power of the acid before we can pronounce upon its strength. (See a paper on the *acetometer*, and the modes of determining the value of acetic acid, by Messrs. J. and P. Taylor.—*Quarterly Journal, O. S.* vi.)

According to Berzelius, whose analysis of acetic acid was very carefully conducted, (THOMSON'S *Annals*, vol. iv.) its ultimate components are

Carbon	46.83
Oxygen	46.82
Hydrogen	6.35
						<hr/>
						100

Gay-Lussac and Thenard, from the analysis of acetate of baryta, estimate the ultimate components of acetic acid as follows:—

Carbon	50.224
Oxygen	44.147
Hydrogen	5.629
						<hr/>
						100

These, and other results which might be quoted, are too much at variance to enable us to determine upon the ultimate composition of the acid; and, in order to ascertain its equivalent number, we must resort to the analysis of the acetates, from which it appears that 50 may be assumed. The theoretical composition of the acid may therefore stand thus,*

4 proportionals of carbon	.	.	24	.	48
3 „ oxygen	.	.	24	.	48
2 „ hydrogen	.	.	2	.	4
			<hr/>	<hr/>	
			50		100

Acetates.—The combinations of acetic acid with the salifiable bases, are all soluble in water, and mostly very soluble: many of them are deliquescent, and difficultly crystallizable; they are decomposed by sulphuric acid; and, when submitted

* According to Dr. Prout, the oxygen and hydrogen in acetic acid are in the proportions that form water; and his analysis would give 51 as the equivalent of the acid, composed of

Carbon	.	.	47.05	=	4 proportionals	.	24
Water	.	.	52.95	=	3 „	.	27
			<hr/>				<hr/>
			100				51

to destructive distillation, some of them furnish a modified vinegar, which has been termed *pyroacetic acid*, and a peculiar inflammable product, which has been termed *pyroacetic ether* or *spirit*: these decompositions have been fully investigated, and the properties of the pyroacetic spirit inquired into, by Mr. Chenevix.—(*Ann. de Chim.*, xlix.)

When distilled off muriate of lime, its specific gravity is .864. It boils at 138°, and leaves no residue when burned. It mixes with water, alcohol, and the volatile oils, in all proportions; and dissolves sulphur, wax, and the fixed oils, when gently heated. It has an acrid taste, and exhales a peculiar odour when burned. It is obtained in considerable quantities during the distillation of wood, and has been used as a substitute for alcohol in lamps; but it exhales a disagreeable smell during combustion.

The following are among the most important of the acetates:—

Acetate of Ammonia is a very deliquescent, soluble salt, and extremely difficultly crystallizable. In solution, obtained by saturating distilled vinegar with carbonate of ammonia, it constitutes the *liquor ammonia acetatis* of the *Pharmacopœia*, which has long been used in medicine as a diaphoretic, under the name of *spirit of Mindererus*. Acetate of ammonia is volatile at 250°, and condenses in crystals. Its theoretical composition is,

Acetic acid	.	.	50	.	.	75
Ammonia	.	.	17	.	.	25
			<hr/>			<hr/>
			67			100

Acetate of Potassa is usually formed by saturating distilled vinegar with carbonate of potassa, and evaporating to dryness. If this salt be carefully fused, it concretes into a lamellar deliquescent mass on cooling. It is the *terra foliata tartari*, and *febrifuge salt of Sylvius*, of old pharmacy. It dissolves in its own weight of water at 60°, and the solution has an acrid saline taste. Boiling alcohol dissolves twice its weight. It consists of one proportional of each of its components, or,

Acetic acid	.	.	50	.	.	51
Potassa	.	.	48	.	.	49
			<hr/>			<hr/>
			98			100

Acetate of Soda forms prismatic crystals, not deliquescent, of an acrid bitterish taste, and soluble in rather less than three parts of water at 60°. It is the *terra foliata crystallisata* of old writers. It consists of

Acetic acid	.	.	.	50	.	.	.	61
Soda	.	.	.	32	.	.	.	39
				<hr/> 82				<hr/> 100

The crystallized salt appears to contain 6 proportionals of water, and to consist, therefore, of

Anhydrous acetate	.	.	.	82	.	.	.	60.7
Water	.	.	.	54	.	.	.	39.3
				<hr/> 136				<hr/> 100

Acetate of Lithia is very deliquescent, and difficultly crystallizable.

Acetate of Lime is a difficultly crystallizable salt, readily soluble in water and alcohol, and of a bitter saline taste. It is sometimes obtained by saturating the vinegar formed during the distillation of wood, and employed by vinegar makers in the preparation of *acetate of alumina*, which is used by the calico printers as a mordant. *Acetate of lime* consists of

Acetic acid	.	.	.	50	.	.	.	64
Lime	.	.	.	28	.	.	.	36
				<hr/> 78				<hr/> 100

Acetate of Baryta furnishes acicular crystals, of a sour and bitterish taste: in cold weather, the concentrated solution congeals into a silky congeries of crystals. It requires rather more than its own weight of water at 60° for solution, and consists of,

Acetic acid	.	.	.	50	.	.	.	39
Baryta	.	.	.	78	.	.	.	61
				<hr/> 128				<hr/> 100

Acetate of Strontia furnishes small permanent crystals, consisting of 50 acid + 52 strontia.

Acetate of Magnesia is uncrystallizable, and of a bitterish sweet taste. It consists of 50 acid + 20 magnesia = 70. It is very soluble in water and alcohol.

Acetate of Manganese formed by dissolving the protocar-

bonate in acetic acid, crystallizes in rhomboidal tables, permanent, and of a reddish colour and astringent metallic taste, soluble in $3\frac{1}{2}$ parts of water at 60° . They consist of 70 acid and water + 30 protoxide of manganese.—JOHN, GEHLEN'S *Journal*, iv.

Acetate of Iron.—The acetic acid combines with both oxides of iron. The *protacetate* is formed by digesting sulphuret of iron in acetic acid; it yields green prismatic crystals, of a styp-tic taste, and readily soluble in water; the solution becomes brown by exposure to air, and passes into *peracetate*, which is uncrystallizable, and obtained by digesting iron in acetic acid. This compound is extensively used by calico printers, who prepare it either by digesting iron in pyroligneous acid, or by mixing solution of acetate of lead with sulphate of iron, and exposing the filtered solution to air.

Acetate of Zinc is formed either by dissolving oxide of zinc in acetic acid, or by mixing a solution of sulphate of zinc with one of acetate of lead. It crystallizes in thin shining plates, of a bitter and metallic taste, very soluble, but not deliquescent. This salt is sometimes used in pharmacy, chiefly as an external application. According to Messrs. Aikin, the specific gravity of a saturated solution of acetate of zinc, made by digesting the salt in distilled vinegar, is 1055. Of this solution, 900 grains contain 53 of dry, or 82.6 of crystallized acetate. One ounce, by measure, of the solution, weighs 506 grains, and contains 29.8 grains of dry, or 46.5 grains of crystallized salt. The theoretical composition of acetate of zinc is,

Acetic acid	.	50	.	53.7
Oxide of zinc	.	42	.	46.3
		<hr/>		<hr/>
		93		100

The crystallized salt contains, according to Thomson, 6 proportionals of water.

Acetate of Tin.—This metal is slowly acted on by acetic acid, but a *protacetate* and *peracetate of tin* may be made by mixing acetate of lead with saturated solutions of the proto-muriate and permuriate of tin. These solutions have been recommended as mordants for the use of dyers. The *protacetate* is crystallizable. Vinegar, kept in tin vessels, dissolves a very minute portion of the metal; and in pewter vessels it likewise

dissolves a small portion of the lead, where in contact both with the vinegar and air; hence, distilled vinegar, which has been condensed in a pewter worm, affords generally traces of both metals.—VAUQUELIN, *Ann. de Chim.*, xxxii.

Acetate of Copper.—By exposing copper to the fumes of vinegar, it becomes gradually incrustated with a green powder called *verdigris*, which is separable by the action of water into an insoluble *subacetate of copper*, and a soluble *acetate*. Common *verdigris* consists, according to Mr. R. Phillips, of

1	proportional of acetic acid	.	=	50
1	„	peroxide of copper	.	= 80
6	„	water	.	= 54
				<hr/>
				184

It is, therefore, *subperacetate of copper*; and, when pure, exists in the form of light-blue silky crystals, separable by the action of water into a soluble and insoluble acetate, the latter of which is decomposed even by cold water, which causes it to assume a brown colour.

Mr. Phillips has given the following comparative statement of the composition of the different kinds of *verdigris*:—

	Blue Crystals.	French Verdigris.	English Verdigris.
Acetic acid	28.30	29.3	29.62
Peroxide of copper	43.25	43.5	42.25
Water	28.45	25.2	27.51
Impurity	0	2.0	0.62
<hr/>			
100 100 100			

Peracetate of Copper may be obtained by digesting *verdigris*, or oxide of copper, in acetic acid; by evaporating this solution, it is obtained in four-sided truncated pyramids of a fine bluish-green tint. It dissolves sparingly in water and alcohol, and communicates a beautiful blue-green colour to the flame of the latter; by distillation it affords a very pure acetic acid. According to Dr. Ure (*Dictionary*—Art. *Copper*), *peracetate of copper*, in its crystallized state, consists of

2	proportionals of acid	.	50 × 2 =	100
1	„	oxide of copper	.	= 80
1	„	water	.	= 9
				<hr/>
				189

Acetate of Lead is the *sugar of lead* and *salt of Saturn* of the old chemists: it may be regarded as the most important of the acetates; it is used in pharmacy, and by dyers and calico

printers for the preparation of acetate of alumina and iron, which are formed by mixing its solution with that of the sulphates of those metals, an insoluble sulphate of lead being at the same time produced. Acetate of lead is formed by digesting the carbonate in distilled vinegar, or in the acetic acid obtained by the destructive distillation of wood: it usually occurs in masses composed of acicular crystals; but by careful crystallization it may be obtained in quadrangular prisms. Its taste is sweet and astringent, and it is soluble in about four parts of water, at 60°. It is sometimes improperly termed a *superacetate*, but the salt is neutral, though when dissolved in water containing the smallest portion of carbonic acid, a white insoluble compound of lead falls, and a little acetic acid being liberated, the solution is rendered sour.

Carbonic acid passed through a solution of acetate of lead, precipitates, according to Mr. South, exactly half the quantity of the oxide which the salt contains; hence a *binacetate* is probably formed, which however does not afford crystals.

According to the experiments of Berzelius, acetate of lead consists of

Acetic acid	26.97
Protoxide of lead	58.71
Water	14.32
	<hr/>
	100

The anhydrous acetate of lead may therefore be regarded as composed of

1 proportional of acetic acid	50	31
1 „ oxide of lead	112	69
	<hr/>	<hr/>
	162	100

and the crystallized acetate, of

Anhydrous acetate	162	85.7
Water (3 proportionals)	27	14.3
	<hr/>	<hr/>
	189	100

When acetate of lead is submitted to destructive distillation it furnishes a considerable quantity of a peculiar fluid, smelling and burning like alcohol.—(PROUST, *Journal de Physique*, tom. lvi.)

Subacetate of lead.—When 100 parts of sugar of lead are boiled in water, with about 150 of yellow oxide, or of finely powdered litharge, a salt is obtained which crystallizes in

plates, and is less sweet and soluble than the acetate; it has been termed *subacetate of lead*, but consists, according to Berzelius, of 1 proportional of acid = 50 + 3 proportionals of oxide of lead, 336. The solution of this compound has long been used in pharmacy, under the name of *Goulard's extract of lead*. It is very rapidly precipitated by carbonic acid, of which it is a most delicate test; it also has a strong attraction for vegetable colouring matter, upon which principle I employed it in my analyses of wines. (*Phil. Trans.*, 1813.)

Acetate of Antimony, formed by digesting the protoxide in acetic acid, was once employed as an emetic.

Acetate of Bismuth may be formed by adding nitrate of bismuth to a concentrated solution of acetate of potassa; a precipitate falls, which redissolves on the application of heat, and afterwards affords scaly crystals. The addition of acetic acid to nitrate of bismuth prevents its precipitation when diluted.—(MORVEAU, *Encyc. Méthod. Chimie*, i. 10.)

Acetate of Cobalt may be obtained by digesting oxide of cobalt in acetic acid; it is uncrystallizable, and furnishes a sympathetic ink, colourless when cold, but blue when heated.

Acetate of Uranium forms four-sided prismatic crystals of a yellow colour.

Acetate of Titanium, not examined.

Acetate of Cerium.—Recently precipitated oxide of cerium readily dissolves in acetic acid, and yields small crystals on evaporation, of a sweetish taste, permanent, and readily soluble in water.—(HISINGER and BERZELIUS, GEHLEN'S *Journal*, ii. 414.)

Acetate of Nickel forms green rhomboidal crystals.

Acetate of Mercury.—*Protacetate of Mercury* is most readily formed by mixing a solution of protonitrate of mercury with acetate of potassa. For this purpose dissolve three ounces of mercury in about four ounces and a half of cold nitric acid, and mix this solution with three ounces of acetate of potassa previously dissolved in eight pints of boiling water, and set the whole aside to crystallize, which takes place as the liquor cools, and the acetate of mercury then separates in the form of micaceous crystalline plates, which are to be washed in cold water, and dried on blotting paper. (*Edinburgh Pharmacopœia*.) In preparing this salt, the quantity of water for

dissolving the acetate need not be so large as above directed, two pints being sufficient, but it is necessary to pour the mercurial solution into the acetate. This salt has an acrid taste, and is very difficultly soluble in water, requiring, according to Braconnot (*Annales de Chimie*, lxxxvi. 92), 600 parts of water. It is insoluble in alcohol. It was once used in medicine.

Peracetate of Mercury is formed by digesting the peroxide in acetic acid ; it does not crystallize, and affords on evaporation a deliquescent yellow mass, which is decomposed by water into a *superperacetate*, which remains dissolved ; and an insoluble *subperacetate*.—(PROUST, *Journal de Phys.*, lvi.)

Acetate of Silver is obtained by boiling the acid on oxide of silver, or by mixing solutions of acetate of potassa and nitrate of silver ; it forms acicular crystals of an acrid metallic taste.

Acetate of Alumina.—This salt is extensively employed by calico printers as a mordant or basis for fixing colours ; they produce it by mixing solutions of alum and acetate of lead : about three pounds of alum are dissolved in eight gallons of water, and a pound and a half of sugar of lead stirred into it ; a copious formation of sulphate of lead ensues, which is allowed to subside, and the clear liquor holding acetate of alumina and a portion of undecomposed alum in solution, is then drawn off, a portion of pearlash and chalk being added to it previous to use, in order to saturate any excess of acid. This salt is also produced by the mutual decomposition of acetate of lime and alum. A gallon of a solution of the acetate, of a specific gravity of about 1.050, equivalent to nearly half a pound avoirdupois of dry acetic acid, is employed for every $2\frac{3}{4}$ lbs. of alum. (URE's *Dictionary*—Art. *Alumina*.)

Acetate of alumina, formed by digesting recently precipitated alumina in acetic acid, may be procured in deliquescent acicular crystals of an astringent taste, and containing, according to Richter, 73.81 acid + 26.19 alumina : hence it is probably a *binacetate*.

The solution of this salt becomes turbid when heated, and again transparent on cooling ; a curious circumstance, first observed by Gay-Lussac, and depending upon a temporary decomposition of the acetate ; whether the deposit be alumina or a subacetate seems not understood ; it is prevented in the solutions used by the calico printer, by excess of alum.

CHAPTER IX.

OF ANIMAL SUBSTANCES.

THE different Sections of this Chapter will contain an account of the ultimate and proximate principles of the substances belonging to the animal creation; of the different methods of analysis by which these principles are obtained; and of such of the animal functions as are concerned in their production, where these are susceptible of chemical elucidation.

Section I. OF THE ULTIMATE PRINCIPLES OF ANIMAL MATTER, AND OF THE PRODUCTS OF ITS DESTRUCTIVE DISTILLATION.

THE proximate principles of the animal creation consist, like those of vegetables, of a few elementary substances, which by combination in various proportions, give rise to their numerous varieties. Carbon, hydrogen, oxygen, and nitrogen, are the principal ultimate elements of animal matter; and phosphorus and sulphur are also often contained in it. The presence of nitrogen constitutes the most striking peculiarity of animal, compared with vegetable bodies; but as some vegetables contain nitrogen, so there are also certain animal principles, into the composition of which it does not enter.

The presence of nitrogen stamps a peculiarity upon the products obtained by the destructive distillation of animal matter, and which are characterized by the presence of ammonia, formed by the union of the hydrogen with the nitrogen. It is sometimes so abundantly generated as to be the leading product; thus, when horn, hoofs, or bones, are distilled *per se*, a quantity of solid carbonate of ammonia, and of the same sub-

stance combined with empyreumatic oil, and dissolved in water, are obtained; hence the pharmaceutical preparations called *spirit* and *salt of hartshorn*, and Dippel's *animal oil*. Occasionally the acetic, benzoic, and some other acids are formed by the operation of heat on animal bodies, and these are found united to the ammonia; cyanogen and hydrocyanic acid also frequently occur.

If the gas evolved during the decomposition of animal bodies be examined, it is generally inflammable, and consists of carburetted hydrogen, often with a little sulphuretted and phosphuretted hydrogen; carbonic oxide, carbonic acid, and nitrogen, are also sometimes detected in it.

The coal remaining in the retort is commonly very difficult of incineration, a circumstance depending upon the common salt and phosphate of lime, which it usually contains, forming a glaze upon its surface which defends the carbon from the action of the air. Animal charcoal is also found to be more effectual in destroying colour and smell, than that obtained from vegetables. (See CARBON, vol. i.)

By the term *putrefaction* we mean the changes which dead animal matter undergoes, and by which it is slowly resolved into new products. These changes require a due temperature, and the presence of moisture; for below the freezing point of water, or when perfectly dry, it undergoes no alteration.

During putrefaction the parts become soft and flabby, they change in colour, exhale a nauseous and disgusting odour, diminish considerably in weight, and afford several new products, some of which escape in a gaseous form, others run off in a liquid state, and others are contained in the fatty, or earthy residuum.

The presence of air, though not necessary to putrefaction, materially accelerates it, and those gases which contain no oxygen are very efficient in checking or altogether preventing the process. Carbonic acid also remarkably retards putrefaction; and if boiled meat be carefully confined in vessels containing that gas, it remains for a very long time unchanged, as seen in M. Appert's method of preserving meat.

There are several substances which, by forming new combinations with animal matter, retard or prevent putrefaction, such as many of the saline and metallic compounds; sugar,

alcohol, volatile oils, acetic acid, and many other vegetable substances also stand in the list of anti-putrefactives, though their mode of operating is by no means understood.

The effluvia which arise from putrescent substances, and more especially those generated in certain putrid disorders, have a tendency to create peculiar diseases, or to give the living body a tendency to produce poisons analogous to themselves. An atmosphere thus tainted by infectious matter, may be rendered harmless by fumigation with the volatile acids, more especially the nitrous and the muriatic; chlorine is, however, more effectual: the vapour of vinegar, though sometimes useful in covering a bad smell, is not to be relied on. It appears evident that the acid and chlorine act chemically upon the pernicious matter, and resolve it into innocuous principles.

When muscular flesh is immersed in a stream of running water, it is partially converted into a substance having many of the properties of fat combined with a portion of ammonia. The same changes have been observed where large masses of putrefying animal matter have been heaped together, or where water has had occasional access to it. Nitrate of ammonia is also sometimes formed under the same circumstances.

Instead of considering the proximate principles of animals under separate sections, as has been done in regard to vegetable bodies, I shall make them known under the heads of those substances in which they occur, the principal of which are the following:—

1. Blood. Albumen. Colouring Matter.
2. Milk. Sugar of Milk.
3. Bile. Resin of Bile.
4. Lymph. Mucus. Synovia. Pus, &c.
5. Urine. Urea. Urinary Calculi.
6. Skin. Membrane.
7. Muscle. Ligament. Horn. Hair.
8. Fat. Spermaceti. Cerebral Substance, &c.
9. Shell and Bone.

I am aware of the imperfections and inconvenience of this arrangement, but in the present state of animal chemistry it is difficult to adopt one liable to fewer objections; indeed our systematic arrangements of organic bodies generally require reconsideration and revision. Gay-Lussac and Thenard, in their *Recherches Physico-Chymiques*, have divided the proxi-

mate principles of animals into three sections. The first contains those which are neither acid nor oleaginous; such as albumen, gelatine, urea, &c.; they abound in carbon, and the hydrogen they contain is in such proportion as to convert the nitrogen into ammonia, and the oxygen into water. The second section includes animal acids; and the third, fatty bodies; but there are certain products which cannot be referred to either of these sections.

Section II. OF THE BLOOD.

IN the higher orders of animals the blood is of a red colour, florid in the arteries, and dingy in the veins. The specific gravity of human blood is liable to some variation. I have found it as low as 1.050 and as high as 1.070, but am unable to refer to any circumstances which might be considered as the cause of this difference.

When blood is drawn from its vessels in the living animal, it soon concretes into a jelly-like mass, which afterwards gradually separates into a fluid *serum*, of a pale straw colour, and a coagulated *crassamentum*, or *cruor*, which is red. The cause of this coagulation is quite unknown.

The specific gravity of the serum of the blood, is upon an average 1.030. It reddens the yellow of turmeric, and changes the blue of violets to green, a property derived from a portion of soda. At a temperature of 160°, it becomes a firm yellowish-white coagulum, resembling in appearance and properties the coagulated white of egg, and, as the principle to which this property is owing is the same in both substances, it has been called *albumen*. Alcohol, and many of the acids, also occasion the coagulation of the serum of blood.

100 parts of human serum contain between eight and nine parts of albumen, rather less than one part of carbonate of soda, and about the same quantity of common salt, the remaining 90 parts being water. These at least are the proportions which my own experiments lead me to believe correct; but

the analysis is involved in so much difficulty that the results can only be considered as approximating to the truth; indeed it is probable that the composition of the serum is liable to variation.

Dr. Marcet and Berzelius have each given an analysis of the serum of human blood; the following are their results. (*Medico-Chirurgical Transactions*, vol. ii. *Annals of Philosophy*, vol. ii.)

MARCET.

Water	900.
Albumen	86.8
Muriates of potassa and soda	6.6
Muco-extractive matter	4.0
Carbonate of soda	1.65
Sulphate of potassa	0.35
Earthy phosphates	0.60
	<hr/>
	1000

BERZELIUS.

Water	905.0
Albumen	80.0
Muriates of potassa and soda	6.0
Lactate of soda, with animal matter	4.0
Soda and phosphate of soda with ditto	4.1
Loss	0.9
	<hr/>
	1000

Albumen, which constitutes a leading ingredient in the serum, and which we shall presently find also in the cruor, is a very important animal principle, and is found in the greater number of animal fluids and solids.

Liquid Albumen is soluble in water, and always contains a notable portion of soda, indicated by its action on vegetable colours. It is coagulated by heat, by certain saline compounds, by most of the acids, and by alcohol, unless it be considerably diluted with water, in which case a portion separates in the form of white flakes after some hours' standing. According to Dr. Bostock, water containing only one thousandth of its weight, becomes turbid on boiling. The facility with which albumen coagulates by heat, renders it applicable to the *clarification* of various liquids, such as syrups, jellies, &c., with which it is mixed in the liquid state of serum or white of egg, and on boiling the mixture, the coagulum which is formed

entangles and absorbs the suspended substances. Solution of corrosive sublimate, added to albumen very much diluted, produces a cloudiness, and hence it is a useful test of albumen. (BOSTOCK, NICHOLSON'S *Journal*, xiv.) Ferrocyanate of potassa is also a delicate test of dissolved albumen, any excess of alkali having been previously removed by a little acetic acid. Dilute muriatic, nitric, sulphuric, and phosphoric acids, coagulate albumen; so do several of the vegetable acids; acetic acid only does so under certain circumstances, and phosphoric acid, which has long been kept in solution, gradually loses its power of acting as a precipitant of albumen.

Liquid albumen is instantly coagulated by Voltaic electricity; and if two platinum wires, connected with a small battery, be immersed into a diluted albumen, it will cause a coagulation at the negative pole, and scarcely any effect at the positive pole. This circumstance induced me to attribute the coagulation to the removal of the alkali, by alcohol, and by acids; but how heat operates is not very obvious, unless we may be allowed to consider it as effecting a kind of decomposition of the liquid albumen. We might thus consider liquid albumen as a compound of albumen and soda dissolved in water: the effect of heat would then be to transfer the soda to the water, and thus occasion a coagulation; and a solution of soda is always found oozing from coagulated serum, and has sometimes been called *serosity*; in time it re-acts upon the coagulum, and dissolves a portion of it.

It must, however, be admitted that this view of the cause of coagulation is not altogether satisfactory. Dr. Turner suggests the following opinion upon the subject:—"That albumen combines directly with water at the moment of being secreted, at a time when its particles are in a state of minute division; but as its affinity for that liquid is very feeble, the compound is decomposed by slight causes; and, for the same reason, the albumen becomes quite insoluble as soon as it is rendered solid by coagulation. Silica affords an instance of a similar phenomenon."

When albumen is dried in a moderate heat, it shrinks and becomes brown and semi-transparent, resembling horn in appearance and properties. In this state it scarcely dissolves in boiling water, though it gradually softens; it is not prone to

decomposition ; it dissolves in the alkalis, a portion of ammonia being evolved and a saponaceous compound formed. Dilute nitric acid converts it into a substance having the properties of gelatine. (HATCHETT, *Phil. Trans.*, 1800.)

By destructive distillation albumen furnishes a variety of products characterized by the presence of a large proportion of ammonia. According to the analyses of Gay-Lussac and Thenard, (*Recherches Physico-Chymiques*,) and of Dr. Prout, its ultimate constituents are

	Gay Lussac & Thenard.	Prout.
Carbon . . .	52.883	50.00
Oxygen . . .	23.872	26.67
Hydrogen . . .	7.540	7.78
Nitrogen . . .	15.705	15.55
	<hr/> 100	<hr/> 100

Fibrine.—When the coagulum of the blood is carefully washed under a small stream of water, the colouring matter is gradually dissolved, and washed out of it, and a white fibrous substance remains, which has been termed *fibrina* or *coagulable lymph*, but of which the essential chemical properties are those of albumen. Acetic acid dissolves it into a gelatinous mass. It is also dissolved and decomposed when boiled in a recent state with nitric acid ; but when dried so as to assume the appearance of horn, and then digested in dilute nitric acid, it becomes gelatinous. Sulphuric acid chars, and ultimately decomposes it ; but if water be added to the recent mixture and a boiling heat applied for a few hours, in separating the acid by chalk a white matter is found in the solution possessed of some peculiar properties, and to which Braconnot has given the name of *Leucine*. (*Ann. de Chim. et Phys.* xiii.)

It sometimes happens, when the blood is long in coagulating, as in certain inflammatory diseases, that a portion of this albumen is left without the colouring matter, forming what has been called *the buffy coat of blood* ; in this case it is so tough as to admit of being removed from the coloured portion, and when dried, shrinks up, and appears exactly like horn.

Although the cause of the spontaneous coagulation of blood be unknown, the process consists in a portion of the albumen separating in a solid form along with the colouring matter,

while another portion remains dissolved in the serum; this effect is somewhat analogous to the crystallization of a saline solution, in which one portion of the salt separates, while another remains dissolved.

The colour of the blood has generally been referred to small globules of a red colour, which, by the aid of the microscope may be discerned in it; and it was supposed that these globules are soluble in water. But it has been shown by Dr. Young, that this is not the case, and that the effect of water is to dissolve the colouring matter only, leaving the globule perfectly colourless; in this state the globular particles have the properties of albumen. The diameter of the globules in human blood varies from $\frac{1}{60000}$ to $\frac{1}{40000}$ of an inch.—*Remarks on Blood and Pus, in Dr. YOUNG'S Medical Literature.*

The colouring matter of the blood can scarcely be obtained free from other substances. By stirring it during coagulation, a considerable portion is diffused through the serum, from which it afterwards subsides. Vauquelin advises the digestion of the coagulum, drained of serum, in dilute sulphuric acid, at a temperature of 160°. The liquid, filtered while hot, is to be evaporated to half its bulk, and nearly saturated with ammonia; the colouring matter falls, and is to be washed and dried. (*Annales de Chim. et Phys.*, tom. i.) We must not, however, trust animal principles to these complex operations; and there can, I think, be little doubt that the colouring principle has undergone some change in M. Vauquelin's process.

The chemical properties of the colouring matter of the blood seem to show that it is a peculiar animal principle. It is soluble in cold water, and the solution, when boiled, deposits a brown sediment of altered colouring matter. Muriatic, dilute sulphuric, and several of the vegetable acids, and the caustic and carbonated alkalis, readily dissolve the colouring matter, and form solutions of different tints of red, and of a peculiar greenish hue when viewed by transmitted light. Nitric acid instantly renders these solutions brown, and decomposes the red principle. These experiments, of which I have given a detailed account in the *Phil. Trans.* for 1812, led me to regard the colouring matter of the blood as a distinct proximate principle of animal matter, independent of the presence of iron, to which metal its peculiarities were at one time re-

ferred by MM. Fourcroy and Vauquelin; and the latter of these celebrated chemists has more lately verified my conclusions in the above-quoted memoir. Berzelius, whose labours in animal chemistry are so extended and well known, has, however, obtained different results; he finds the crassamentum of the blood to consist of

Colouring matter	.	.	.	64
Fibrin and albumen	.	.	.	36
				<hr/>
				100

The colouring matter, when incinerated, affords a residue consisting of

Oxide of iron	.	.	.	50.0
Subphosphate of iron	.	.	.	7.5
Phosphate of lime with magnesia	.	.	.	6.0
Lime	.	.	.	20.0
Carbonic acid and loss	.	.	.	16.5
				<hr/>
				100

The iron appears to be regarded by Berzelius as contributing to the red colour of the blood, a conclusion which my own experiments, detailed in the paper already quoted, by no means warrant, and which is also at variance with the opinion of M. Vauquelin. A hint has lately been thrown out by Dr. Ure as to the possibility of the colour of the blood being derived from sulphocyanate of iron. (See *Saliva*.)

Besides the principles now enumerated, and which may be considered as essential to the blood, it often contains carbonic acid, which escapes when the blood is gently heated, or placed under the exhausted receiver of the air-pump.

Experiments on the blood, in different diseases, have thrown no light whatever on their nature, nor have any material differences been found in the blood of the same animal at different periods, or in that of different animals of the same class. Upon these subjects the reader is referred to a memoir on the blood by MM. Prevost and Dumas. (*Annales de Chim. et Phys.*, xxiii., *Quart. Journ.*, xvi., 115.)

The following curious facts respecting the odour of different kinds of blood have been announced by M. Baruel.

Whilst preparing the colouring matter of blood according

to M. Vauquelin's process, the clot of ox blood was heated with a large excess of sulphuric acid of moderate strength, on which occasion a strong odour of beef was observed. Some time after, having occasion to operate upon the blood of a man who had taken opium, the fluid was first coagulated by heat, and divided, after which it was boiled with weak sulphuric acid: immediately so strong an odour of the sweat of man was evolved as to infect the whole laboratory, and render it necessary for the persons to leave the place. This and the former fact combined, induced M. Baruel to extend his experiments on these subjects, and the following are the results.

i. The blood of each species of animal contains a principle peculiar to each. ii. This principle, which is very volatile, has an odour resembling that of the sweat, or the cutaneous or pulmonary exhalation of the animal from which the blood was taken. iii. In the blood this volatile principle is in a state of combination, its odour being then insensible. iv. When the combination is broken, this principle is volatilized, when it is easy to recognize the animal to which it belongs. v. In each species of animal, this principle is more decided, or has more intensity of odour in the male than in the female; and in men, the colour of the hair accompanies certain variations in this principle. vi. This principle is in a soluble state in the blood, and may be found, therefore, either in the unaltered blood, or after the fibrine has been removed, or even in the serosity of blood. vii. Of all the means of separating this principle, concentrated sulphuric acid has succeeded best.

To obtain these results, it is only necessary to put a few drops of blood, or the serum of blood, into a glass, to add concentrated sulphuric acid to the amount of one-third or half as much as of blood, and to stir the whole together with a tube—the odoriferous principle is immediately rendered evident. By these means, M. Baruel can readily distinguish the blood from the following sources.

i. That of a man disengages a strong odour of the perspiration of man, which it is impossible to confound with any other. ii. That of a woman, a similar odour, much weaker, and resembling the perspiration of women. iii. That of the ox, a strong odour of beef. iv. That of the horse, a strong

odour of the perspiration of the horse. v. That of the sheep, a strong odour of wool, impregnated with the perspiration of that animal. vi. That of the dog, the odour of the transpiration of a dog. vii. That of a pig, the disagreeable odour of a piggery. viii. That of a rat, the bad odour belonging to the rat.

The same result has been obtained with the blood of various kinds of birds, and even with the blood of a frog, which gave the strong odour of marshy reeds, &c., and with that of a carp, which gave a principle smelling like the mucus which covers the bodies of fresh-water fish.

Upon trials made to ascertain whether spots of blood could be distinguished, and referred to their source, M. Baruel found, that to a certain extent, a pretty sure judgment could be given, even after fifteen days or more. The spotted linen is to be cut out, put into a watch-glass, and being moistened with a little water, is to be left for a short time at rest. When well moistened, a little concentrated sulphuric acid is to be added, and stirred about with a tube; then, by respiring near it, the odour may be perceived. M. Baruel is not sure that the distinction could be ascertained after more than fifteen days, and therefore recommends legal officers to allow of no delay in any experiments, which bear upon cases of judicial investigation.

Section III. MILK.

THE chemical properties of this secretion differ somewhat in different animals. The milk of the cow has been most attentively examined, and it has the following properties:—

It is nearly opaque; white, or slightly yellow; of an agreeable sweetish taste, and a peculiar smell. Its specific gravity varies from 1.018 to 1.020. It boils at a temperature a little above that of water, and freezes at 32°. When allowed to remain a few hours at rest, a thick unctuous liquid collects upon its surface, called *cream*; the colour of the remaining

milk becomes bluish-white, and when heated to about 100° with a little *rennet*, it readily separates into a *coagulum* or *curd*, and a *serum* or *whey*. In this way the three principal constituents of milk are separable from each other.

By the process of churning, cream is separated into *butter* and *butter-milk*, the latter being the whey united to a portion of curd. According to Berzelius, 100 parts of cream, of the specific gravity of 1.024, consist of

Butter	4.5
Curd	3.5
Whey	92.0
						<hr/> 100

Butter may be considered as an animal oil, containing a small portion of curd and whey. It liquefies at about 98° , and by this process the impurities are separated, and it remains a longer time without becoming rancid. 100 parts of alcohol, specific gravity .822, dissolve 3.46 of butter.

The *curd* of milk has the leading properties of coagulated albumen; and, like that principle, is coagulable by alcohol and acids, and is also similarly affected by voltaic electricity; heat slowly produces the same effect; and, by boiling milk, the albumen separates in successive films.

Curd, in combination with various proportions of butter, constitutes the varieties of *cheese*; that containing the largest quantity of oil becomes semi-fluid when heated; it is prone to decomposition, and a large quantity of ammonia is then formed in it; whereas bad cheese, which consists of little else than curd or albumen, shrinks and dries when heated, curling up like a piece of horn.

Whey is a transparent fluid, of a pale yellow colour, and a sweetish flavour; by evaporation, it affords a minute quantity of saline matter, and a considerable portion of sugar of milk.

I must here refer the reader to Chevreul, Prout, Braconnot, Berzelius, and to such elementary writers as have quoted and abridged their experiments, for an account of the *butyric*, *capric*, *caproic*, *caseous*, and *caseic acids*; and of *aposepidine*, and *glycerine*, and several other substances existing, or supposed to exist, in butter and cheese, but which appear to me not to have been sufficiently investigated to entitle them to a regular place in a chemical arrangement.

Sugar of Milk may be obtained in white rhomboidal crystals, of a sweet taste, and soluble in seven parts of water at 60°, but insoluble in alcohol. When exposed to heat, it affords nearly the same products as common sugar. It consists, according to Berzelius, when deprived of water, of

Carbon	45.267
Oxygen	48.348
Hydrogen	6.385
					<hr/>
					100

Dr. Prout has also analyzed sugar of milk, rendered as pure as possible by repeated crystallizations, and freed from its hygrometric moisture by confinement under a receiver with sulphuric acid; it was found to consist of

Carbon	40
Water	60

Saccholactic Acid.—When sugar of milk is treated with nitric acid, it affords a peculiar acid, similar to that above-mentioned, as obtained from gum. To procure this acid, one part of powdered gum arabic may be digested in two of nitric acid, in a moderate heat; as soon as effervescence commences, set the flask in a cool place, and a quantity of white powder subsides, which is to be collected upon a filter, digested in dilute nitric acid to separate oxalate of lime, and subsequently purified by boiling water, which deposits the *mucic* or *sacclactic acid* on cooling. If sugar of milk be used instead of gum, it is obtained pure by the first operation. This acid is not crystallizable, and is sparingly soluble in water, requiring 60 parts, at 212°, and is deposited as the solution cools, in the form of a white gritty powder, of a slightly acid taste. It combines with the metallic oxides, and forms a class of salts called *saccholates*, or *sacclactates*. It consists, according to Berzelius, (*Annals of Philosophy*, vol. v.) of

Carbon	.	.	.	33.430
Oxygen	.	.	.	61.465
Hydrogen	.	.	.	5.105
				<hr/>
				100

Dr. Prout has given the following method of purifying the sacclactic acid, as prepared from gum, and its analysis.—(*Phil. Trans.*, 1827.)

Add ammonia, in slight excess, to the impure acid, and afterwards as much boiling distilled water as will dissolve the saclactate formed. Filter the solution while boiling hot, and then evaporate it very slowly nearly to dryness. The saclactate of ammonia will be separated in the form of crystals, which are to be washed with cold distilled water till they become quite white and pure. They are now to be again dissolved in distilled water, and the boiling saturated solution permitted to drop from a filter into cold diluted nitric acid. This latter, of course, decomposes the saclactate, and precipitates the saclactic acid in a state of perfect purity. Thus obtained, this acid was found to consist of

Carbon	33.33
Water	44.44
Oxygen	22.22

results differing a little from those of other chemists, who probably did not take the necessary pains to obtain this acid in a perfectly pure state.

The *saccholates*, or *saclactates*, have scarcely been examined. With ammonia, potassa, and soda, this acid forms crystallizable compounds, more soluble than the acid. The saclactates of lime, baryta, and strontia, are insoluble, as are those of silver, mercury, and lead.

When milk or whey are exposed to a temperature between 60° and 80°, they undergo a spontaneous change, attended by the production of an acid, which was originally examined by Scheele, and has been termed *lactic acid*. Fourcroy and Vauquelin have shewn reason to suspect its peculiar nature, and were led to regard it as identical with the acetic acid. Berzelius has more recently revived the opinion of Scheele; but I am induced, from my own experiments, to believe, that if it be not the acetic acid originally, it becomes so by combination with a base, and subsequent separation by sulphuric acid.

In some cases, whey may be made to undergo vinous fermentation; and the Tartars, it is said, prepare a kind of wine from the whey of mares' milk, which they call *Koumiss*.—(*Edinburgh Phil. Trans.* vol. ii.)

Section IV. BILE.

THIS secretion is formed in the liver, from venous blood. It is an unctuous liquid, of a yellowish-green colour, and its specific gravity is between 1.020 and 1.030. Its taste is intensely bitter, and it readily putrefies, exhaling a most nauseous odour.

When the bile of the ox is distilled, it affords about 90 *per cent.* of insipid water; the residuum is brown, bitter, and may be redissolved in water; it affords traces of uncombined alkali, which appears to be soda. The acids render bile turbid, and separate from it a substance which possesses many of the properties of albumen. It is likewise coagulated by alcohol, and upon filtering off the clear liquor and evaporating it, an inflammable fusible substance is obtained, of an intensely bitter flavour, combined with a portion of soda and common salt: this has been termed the *resin of bile*, and appears to be the principle which confers upon it its chief peculiarities. We should therefore conclude, as the result of these observations, that bile consists of water, albumen, soda, a bitter resin, and some minute portions of saline matter*.

Thenard separated from bile a peculiar substance, which he has termed *picromel*; but the process by which he obtained it is so complex, that I think it doubtful whether it be a product or an educt. The same chemist has given the following table of the ingredients of ox-bile, but as this secretion is liable to considerable variation in appearance and specific gravity, it is probable that little reliance can be placed in the accuracy of the numbers (*Traité de Chimie*, tom iii., p. 556.):—

* The first rational experiments upon the chemical nature of bile and of urine, in reference to the treatment of disease, will be found in a "Treatise on Gravel and Gout," by Murray Forbes, London, 1793; in which much that has been subsequently written upon those subjects is anticipated.

Water	700
Resin	15
Picromel	69
Yellow matter	4
Soda	4
Phosphate of soda	2
Muriates of soda and potassa	3.5
Sulphate of soda	0.8
Phosphate of lime and of magnesia	1.2
Oxide of iron	a trace
	<hr/> 1000

Biliary Calculi are of two kinds ; those which most commonly occur, are soft, fusible, of a crystalline texture, and inflammable. They have generally been considered as closely resembling spermaceti ; they are soluble in boiling alcohol, in ether, and difficultly in oil of turpentine. Chevreul, having remarked some peculiarities in this substance, is induced to regard it as a peculiar animal principle, and distinguishes it by the name of *cholesterine*.

Cholesterine is fusible at 280° , and on cooling concretes into a crystalline mass ; rapidly heated to about 400° , it evaporates in dense smoke ; it is insoluble in water, and nearly so in cold alcohol ; boiling alcohol dissolves about one-twentieth its weight. It is soluble in nitric acid ; but not convertible into soap by the alkalis.

The other kind of biliary calculus resembles inspissated bile in appearance, but differs from it in being insoluble in alcohol and water. It is often mixed with variable proportions of the former, constituting biliary calculi of intermediate characters.

The gall-stone of the ox is nearly insoluble in water and alcohol, and appears to consist chiefly of the yellow matter of bile ; painters sometimes use it as a yellow pigment.

M. Bizio found in the gall-bladder of a person who died of jaundice, a fluid perfectly different from bile, from which he obtained a peculiar crystallizable substance, affording, when heated, a purple vapour ; he calls this substance *Erithrogene*. (*Quarterly Journal*, xvi. 173.)

Section V. LYMPH, SALIVA, MUCUS, PUS, ETC.

THE liquid which lubricates the different cavities of the body, which is contained in the lymphatics, and which occasionally forms the chief contents of the thoracic duct, has been termed *lymph*. It is colourless, transparent, miscible in all proportions with water, does not affect vegetable blues, is not coagulated by acids or alcohol, but only rendered slightly turbid by the latter. It has the characters of a very weak solution of albumen.

The fluid which collects in cases of dropsy and in vesications, is of a similar nature, but the proportion of albumen is liable to variation, and hence it is differently influenced by tests; when very rapidly thrown out from inflamed surfaces, it sometimes furnishes a coagulum, apparently as abundant as that of the serum of the blood.

The term *mucus* has sometimes been applied to these fluids, when they have undergone a certain degree of inspissation; at other times, it has been used to designate a very alkaline albuminous fluid. Dr. Bostock has pointed out some circumstances in which mucus differs from liquid albumen, and has proposed subacetate of lead as a test of its presence. (NICHOLSON'S *Journal*, vol. xi.) But that salt is so easily decomposed by many vegetable and animal substances, as to render it of doubtful efficacy for this purpose.

Saliva consists, according to Dr. Bostock (NICHOLSON'S *Journal*, vol. xiv.) of

Water	80
Coagulated albumen	8
Mucus	11
Saline substances	1
						<hr/> 100

I found that it was copiously coagulable by the action of Voltaic electricity, and was hence induced to consider the mucus as a peculiar albuminous combination, not coagulable by the usual means.—(*Phil. Trans.*, 1809.)

We owe to Gmelin the curious discovery of the existence of sulphocyanate of potassa in human saliva. It may be detected

by adding a drop or two of permuriate of iron to saliva, and then diluting it with a little water : in a short time the characteristic red colour of sulphocyanate of iron becomes apparent. In the dog, and in some graminivorous animals, the sulphocyanic acid is combined with soda.

Salivary Concretions of the human subject are generally analogous in composition to bone. A salivary concretion from a horse, analyzed by M. Lassaigne, afforded carbonate of lime 84, phosphate of lime 3, animal matter 9, water 3, loss 1.—The same chemist has also examined the saliva of the horse. (*Annals de Chim. et Phys.*, xix. 174.)

The *Pancreatic Juice* has not been minutely examined, but from the experiments of Dr. Fordyce, it would appear to differ little from saliva, but it contains no sulphocyanate.

Tears contain a small portion of albumen combined with soda, muriate of soda, and water. There are also small portions of other salts.

The *Humours of the Eye*.—The *aqueous* and *vitreous humours* are composed of water holding a minute quantity of albumen and saline matter in solution ; the *crystalline lens* also contains more than half its weight of water, the remainder being an albuminous substance with traces of muriates*.

Synovia is the fluid which lubricates the surfaces of joints. It contains, according to Mr. Hatchett (*Phil. Trans.*, 1799), a small portion of phosphate of lime, and of phosphate of soda and ammonia ; the animal principle appeared to be albumen.

Pus is a term applied to a variety of secretions from abscesses and ulcerated surfaces. When it indicates a healing sore, it has been called *healthy pus*, and has the following properties. It has the consistency of cream, a yellowish colour, and exhibits, under the microscope, the appearance of globules diffused through a fluid. (HOME, *On Ulcers*, 2d Edit., p. 13.) Its specific gravity is about 1.030. It does not affect vegetable colours till it has been some time exposed to air, when it becomes slightly sour ; it does not easily mix with water, alcohol, or dilute acids.—(See Dr. PEARSON'S *Experiments on Pus*, NICHOLSON'S *Journal*, xxx.)

* See an Analysis of the Humours of the Eye, by Berzelius.—*Ann. de Chim. et Phys.*, v.

Section VI. URINE, URINARY CALCULI, ETC.

THIS secretion presents, perhaps, greater difficulties to the analytical chemist, than any other animal product; it is extremely complex, and subject to constant change in the proportions of its components, and in disease several new substances make their appearance.

The chemical history of the urine is of the utmost importance to the medical practitioner; it teaches the nature of the substances which occasionally predominate, so as to constitute *gravel* and *calculi*; and shews the means of influencing and modifying its composition.

The general characters of the urine are too well known to need description. Its specific gravity is of course liable to much variation even in the healthy state, fluctuating between 1.005 and 1.040. The average is about 1.020.

The substances that are always found in urine are, according to my own experiments, the following:—

1. Water.
2. Carbonic acid.
3. Phosphoric acid.
4. Uric acid.
5. Phosphate of lime.
6. Phosphate of ammonia.
7. Phosphate of soda.
8. Phosphate of magnesia.
9. Common salt.
10. Sulphate of soda.
11. Albumen.
12. Urea.

To these Dr. Henry adds,—

13. Fluoric acid.
14. Benzoic acid.
15. Acetic acid.
16. Gelatine.
17. Acetate of ammonia.
18. Sulphate of potassa.
19. Fluuate of lime.
20. Muriate of ammonia.
21. Sulphur.
22. Silica.

But I must here press upon the student's attention, the extreme facility with which the composition of urine is modified and affected by slight causes, and with which its ultimate elements assume new proximate arrangements.

The existence of free acid in recently voided urine is easily demonstrated by its property of reddening vegetable blues, and it performs the important office of retaining some of the difficultly soluble salts in permanent solution ; so that whenever this natural acidity is diminished, the urine has a tendency to deposit the earthy phosphates.

The presence of *carbonic acid* may be shown by placing urine under the receiver of the air-pump ; during exhaustion it escapes, sometimes copiously, but at other times in minute quantities only.

The free *phosphoric acid* may be shewn by the addition of carbonate of lime, a portion of which is converted into phosphate of lime.

Uric Acid is one of the peculiar characteristics of the urine ; its presence may be shewn by evaporating urine to half its bulk, which produces a precipitate consisting of phosphate of lime and uric acid ; the former may be dissolved by dilute muriatic acid, which leaves the latter in the form of a reddish powder. This acid has been very ably examined by Dr. Henry, who made it the subject of a thesis published in 1807 : Dr. Prout has also given much valuable information in relation to it.

Uric acid, called sometimes *lithic acid*, as constituting the principal ingredient in certain urinary calculi, may be abundantly obtained by digesting such calculi in caustic potassa, filtering the solution, and adding excess of muriatic acid, which causes a precipitate of uric acid, which is to be washed with warm water, and dried.

Uric acid, thus obtained, is a grey powder, of scarcely any taste, and requiring, according to Dr. Henry, 1720 parts of water at 60°, and 1150 parts at 212° for solution. It reddens infusion of litmus, and readily dissolves in caustic potassa and soda ; it is sparingly soluble in ammonia, and insoluble in the alkaline carbonates.

According to Dr. Prout, uric acid requires at least 10,000 parts of water at 60° for its solution, but urate of ammonia requires only about 480 times its weight at the same tempera-

ture, and affords a precipitate of uric acid, on the addition of any other acid; for these, among other reasons, Dr. Prout regards urate of ammonia, and not pure uric acid, as existing in urine.

Uric acid dissolves in nitric acid, and upon evaporation a residuum of a fine red tint is obtained, which is peculiar to this combination, and which Dr. Prout has lately shown to possess distinct acid properties; he has called it *purpuric acid*.—(*Phil. Trans.*, 1818.)

The process for obtaining purpuric acid, given by Dr. Prout, is as follows: dissolve *pure* uric acid in dilute nitric acid, and saturate the excess of nitric acid in the solution by ammonia; then evaporate slowly, and red crystals will be separated, consisting of *purpurate of ammonia*; digest these in liquid potassa till the red colour disappears, and then add sulphuric acid in quantity sufficient to saturate the potassa; the purpuric remains in the form of a yellowish powder, without smell or taste, and nearly insoluble in water, alcohol, and ether, but soluble in the concentrated mineral acids. It combines with metallic oxides, and expels carbonic acid from the alkaline carbonates, when aided by heat.

Purpurate of ammonia crystallizes in four-sided prisms of a deep red colour, soluble in about 1500 parts of cold water; the solution is of a fine red.

Purpurate of potassa is more soluble; of *soda* less so.

Purpurate of lime, strontia, and baryta, are nearly insoluble; but *purpurate of magnesia* is very soluble.

It is probable that some of the red sediments of urine, generally attributed to pure uric acid, may contain purpuric acid. The *Rosacic acid* of Proust, obtained by acting upon the red sediment of urine with alcohol, also bears analogy to some similar combination.

According to Dr. Brugnatelli, a new salifiable base is produced by acting upon uric acid by certain other acids. When concentrated sulphuric acid, for instance, is added to uric acid, so as to form a thick paste, it occasions liberation of gas, and a peculiar odour: if water be then added, the mass becomes white, and deposits a solid matter, which is a sulphate of the new base, and which may be obtained in a separate form by decomposing this sulphate by alkaline carbonates; muriatic acid also produces it, constituting a more soluble muriate; acetic acid

requires heat to form it, and nitric acid produces it along with other products, during its violent action. Obtained in a separate form by acting upon the above acid compounds by alkaline carbonates, it appears in the form of a flocculent substance, without taste or smell; slightly soluble in water and alcohol, and distinguished when in acid solution by giving an azure precipitate with ferrocyanate of potassa; the neutral compounds do not produce this effect. It combines with iodine; and by fusion with sulphur and phosphorus. It is not easily decomposed by heat. (*Giornale di Fisica*, iii. 464.)

When uric acid is submitted to destructive distillation, it affords carbonate of ammonia, and a peculiar compound, which sublimes in crystals, and which, according to Dr. Henry, consists of a peculiar acid, *pyrouric acid*, united to ammonia; a quantity of charcoal remains in the retort. The ultimate constituents of uric acid, according to Dr. Prout, are

1	proportional of nitrogen	.	.	14
2	„ carbon	.	.	12
1	„ oxygen	.	.	8
1	„ hydrogen	.	.	1
				<hr/> 35

The *urates* have principally been examined by Dr. Henry, and an account of many of them is given in his *thesis* above quoted.

Phosphate of Lime may be precipitated from urine by the addition of ammonia; its relative quantity is liable to much fluctuation; sometimes it becomes so great as to be deposited as the urine cools, constituting what has been termed *white sand*.

The *Phosphates of Ammonia*, of *Soda*, and of *Magnesia*, and *common Salt*, constitute the principal crystallizable salts contained in the urine; the first of these is probably in great part produced during evaporation, for the saline mass obtained by inspissating urine is no longer acid; the carbonic having escaped, and the phosphoric being saturated by ammonia. The *microcosmic salt*, or *fusible salt of urine*, of the old chemists, is chiefly phosphate of ammonia with a little phosphate of soda, or perhaps a triple *ammonia-phosphate of soda*.

The *Ammoniaco-magnesian Phosphate* is a common, and almost constant ingredient in the urine. It forms a part of the

white sand voided in certain calculous affections, and is sometimes formed in a film upon the surface of the urine, having been held in solution by carbonic acid, and being deposited as that gas escapes.

The existence of *sulphuric acid*, probably combined with *soda*, and perhaps also with *potassa*, may be detected in urine by the addition of nitrate of baryta, which occasions a precipitate of sulphate of baryta.

As urine blackens silver, it has been said to contain *sulphur*; but this is not the case with recent urine, and when it becomes slightly putrid it evolves a little sulphuretted hydrogen.

The existence of *albuminous matter* in urine is sometimes easily demonstrated; at others, the secretion seems not to contain it. It has been said by Mr. Cruikshank, that the urine in some dropsical cases contains so much albumen as to be coagulable by heat (*Phil. Mag.*, vol. ii.) ; but if that ever be the case, the secretion could hardly be called urine. It seems questionable whether the albumen of urine should not sometimes be regarded as derived from the mucous secretion of the bladder. Dr. Prout, in his *Inquiry into the Nature and Treatment of Gravel*, &c., has described some cases of albuminous urine, and has adverted to its method of cure.

Urea is the principle which confers upon urine its chief peculiarities. It may be obtained by slowly evaporating urine to the consistency of syrup; on cooling it concretes into a saline mass, which, by digestion in alcohol, furnishes urea. By carefully distilling off the alcohol, the urea remains in the form of a brown crystallized mass, which, by purification, furnishes colourless prismatic crystals. Or, concentrated nitric acid may be added to the brown urea, which forms with it a crystallized mass, which, after having been washed with a little cold water, is to be dried by pressure in blotting paper. The nitrate of urea thus formed is to be decomposed by neutralizing it with a strong solution of carbonate of potassa, and the solution set aside after having been duly evaporated, to separate the nitre by crystallization. The mother liquor, which is an impure solution of urea, is mixed with animal charcoal into a paste, which, after some hours, is lixiviated with cold water; the urea is dissolved, and the solution evaporated to dryness, at a low temperature. The residue is then digested in pure alcohol,

which deposits crystals of urea on cooling. (PROUT, *Med. Chir. Trans.*, viii.)

Other processes have been given for obtaining urea, which are, I think, objectionable, on account of their complexity; indeed it is doubtful whether, by the action of heat, acid, and alcohol, it is not somewhat altered.

Urea is very soluble; water, at 60°, takes up about its own weight, and boiling water appears to dissolve it in any quantity, and without alteration: boiling alcohol takes up its own weight, and on cooling the urea separates in crystals. Sulphuric ether scarcely dissolves an appreciable portion. Nitric acid produces a crystalline precipitate in the aqueous solution of urea, consisting of the two substances, according to Dr. Prout, in the following proportions:

Nitric acid	47.37
Urea	52.63
						<hr/> 100

A very similar compound may also be produced with oxalic acid.

The fixed alkalis decompose urea, and occasion the evolution of ammonia and some other products. It is to this substance that the copious production of volatile alkali, during the destructive distillation of urine, is referable; and the ammonia which is found in combination with the acids, in putrid urine, is derived from the same source.

Urea combines with most of the metallic oxides; with oxide of silver the compound is grey, and it decomposes with detonation when heated.

According to Dr. Prout's analysis (HENRY'S *Elements*, vol. ii. p. 327), urea consists of

Oxygen	.	26.66	=	1	proportional
Nitrogen	.	46.66	=	1	"
Carbon	.	19.99	=	1	"
Hydrogen	.	6.66	=	2	"

In some diseased states of the urine there is a morbid excess of urea, which may be detected by putting a little of the urine into a watch-glass, and carefully adding an equal quantity of nitric acid, in such a manner that the acid shall subside to the lower part of the glass; if spontaneous crystallization take place, it indicates excess of urea.—PROUT, *on Gravel, &c.*, p. 10.

During the mutual action of ammonia and cyanic acid, a substance has been obtained by Wöhler, having the leading characters of urea. (*Quarterly Journal, N. S.*, iii. 491.)

Such are the properties of the principal ingredients in human urine, to which several others have been added by different chemists; but as their existence is only occasional, and often, I think, doubtful, I have hesitated to give them a place among the regular constituents of healthy urine. I now subjoin Berzelius's statement of the average composition of human urine.—(THOMSON'S *Annals*, vol. ii. p. 423.)

Water	933.00
Urea	30.10
Sulphate of potassa	3.71
Sulphate of soda	3.16
Phosphate of soda	2.94
Muriate of soda	4.45
Phosphate of ammonia	1.65
Muriate of ammonia	1.50
Free lactic acid (acetic)	17.14
Lactate of ammonia (acetate)	
Animal matter soluble in alcohol	
Urea not separable from the preceding	1.00
Earthy phosphates, with a trace of fluuate of lime	
Uric acid	1.00
Mucus of the bladder	0.32
Silica	0.03
<hr/>	
1000	

The urine suffers some very remarkable changes in certain diseases, which have been but superficially inquired into by chemists. In cases of injury of the spine, affecting the nerves that supply the kidneys, the urine is always turbid, and often alkaline; and there is a considerable tendency in these cases to form calculi.

In the disease called *diabetes*, the urine is not only secreted in excess, but often contains a substance of a sweet taste, having the properties of sugar, and its specific gravity is considerably above the healthy standard. (HENRY, *on Diabetic Urine. Medico-Chirurgical Trans.*, vol. ii. p. 118.) The following Table, constructed by Dr. Henry, shows the quantity of solid extract in a wine-pint of urine, of different specific gravities, from 1.020 to 1.050. In the experiments which furnished the data of this table, the urine was evaporated by a steam heat

till it ceased to lose weight, and left an extract, which became solid on cooling.—(PROUT, *on Gravel*, p. 62.)

Specific gravity compared with 1000 parts of water at 60°.	Quantity of solid extract in a wine-pint.	Quantity of solid extract in a wine-pint, in			
	grs.	oz.	dr.	scr.	grs.
1020	382.4	0	6	1	2
1021	401.6	0	6	2	1
1022	420.8	0	7	0	0
1023	440.0	0	7	1	0
1024	459.2	0	7	1	19
1025	478.4	0	7	2	18
1026	497.6	1	0	0	17
1027	516.8	1	0	1	16
1028	536.0	1	0	2	16
1029	555.2	1	1	0	15
1030	574.4	1	1	1	14
1031	593.6	1	1	2	13
1032	612.8	1	2	0	12
1033	632.0	1	2	1	12
1034	651.2	1	2	2	11
1035	670.4	1	3	0	10
1036	689.6	1	3	1	9
1037	708.8	1	3	2	8
1038	728.0	1	4	0	8
1039	747.2	1	4	1	7
1040	766.4	1	4	2	6
1041	785.6	1	5	0	5
1042	804.8	1	5	1	4
1043	824.0	1	5	2	3
1044	843.2	1	6	0	3
1045	862.4	1	6	1	2
1046	881.6	1	6	2	1
1047	900.8	1	7	0	0
1048	920.0	1	7	1	0
1049	939.2	1	7	1	19
1050	958.4	1	7	2	18

The urine of graminivorous animals differs considerably from that of the human subject. Carbonates, muriates, and phosphates, are the leading ingredients; it also contains urea, but not uric acid; potassa is usually the predominating alkali. In the *Phil. Trans.* for 1808, I have given an account of the

composition of several species of urine, and in that of the camel I detected a small portion of uric acid: but as the animal was diseased, its presence was probably accidental, more especially as it has not been found by other chemists.

In the urine of the snake, and of most birds that feed upon fish and animal matter, uric acid is the leading ingredient. It is also abundant in the excrement of the parrot, and of other birds which feed upon vegetables only.—(J. DAVY, *Phil. Trans.* 1821.)

Urinary Sand, Gravel, and Calculi.—It frequently happens, from a variety of causes, that certain ingredients of human urine are secreted in excess, and deposited in a solid form, constituting *sand*, or *gravel* and *calculi*.

Sand is either *white* or *red*; the former consists of phosphate of lime, and ammoniaco-magnesian phosphate, either separate or mixed: and the latter is chiefly uric acid. The former deposition is prevented by the use of acids; and the latter by alkalis and the alkaline earths. The modes of exhibiting these remedies, and the effects which they produce, I have described in a paper printed in the *Quarterly Journal of Science and Arts*, vol. vi.

Urinary calculi are, for the most part, composed of materials that exist at all times in the urine, though there are a few substances that only make their occasional appearance in them. The following are their component ingredients:—

1. Uric or lithic acid.
2. Urate of ammonia.
3. Phosphate of lime.
4. Ammonio-magnesian phosphate.
5. Oxalate of lime.
6. Cystic oxide.
7. Carbonate of lime.
8. Silica.*

* Dr. Yellowly, in a paper on "The Tendency to Calculous Diseases," published in the *Phil. Trans.* for 1828, has given the following view of the proportions of the different descriptions of calculi contained in the collection belonging to the Norwich Hospital.

Calculi consisting principally of one deposit.

Lithic acid	81
Lithate of ammonia	20
						Oxalate	

The calculi composed of uric acid, of which the chemical properties have already been described, are of a brown or fawn

Oxalate of lime	20
Phosphate of lime	4
Fusible calculus, or mixed phosphates; that is to say, calculi composed of the triple, or ammoniaco-magnesian phosphate, united with phosphate of lime	37

Calculi consisting of two deposits.

Lithic acid and lithate of ammonia	37
" oxalate of lime	11
" mixed phosphates	10
" phosphate of lime	2
Lithate of ammonia and lithic acid	2
" oxalate of lime	25
" mixed phosphates	14
" phosphate of lime	1
Oxalate of lime and lithic acid	10
" lithate of ammonia	1
" mixed phosphates	15
" phosphate of lime	3
Mixed phosphates and phosphate of lime	2

Calculi consisting of three deposits.

Lithic acid, phosphate of lime, and mixed phosphates	2
" oxalate of lime, and phosphate of lime	1
" oxalate of lime, and lithate of ammonia	2
" oxalate of lime, and lithic acid	4
" lithate of ammonia, and oxalate of lime	2
" oxalate of lime, and mixed phosphates	1
Lithate of ammonia, oxalate of lime, and mixed phosphates	3
" oxalate of lime, and lithic acid	8
" phosphate of lime, and lithate of ammonia	1
" lithic acid and mixed phosphates	2
Oxalate of lime, lithic acid, and lithate of ammonia	1
" lithic acid, and oxalate of lime	1
" lithic acid, and mixed phosphates	2

Calculi consisting of four or more deposits.

Lithate of ammonia, oxalate of lime, lithic acid, and mixed phosphates	1
Oxalate of lime, lithic acid, oxalate of lime, and mixed phosphates	1
Lithate of ammonia, oxalate of lime, phosphate of lime, oxalate of lime, and lithate of ammonia	1

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In this table it will be seen that about one half of the specimens are composed of one description of material only; and that the remainder consist of alternating layers, more or less numerous, of most of the substances of which human urinary calculi are composed.

colour ; and, when cut through, appear of a more or less distinctly laminated texture. Their surface is generally smooth, or nearly so, being sometimes slightly tuberculated. Before the blow-pipe, this calculus blackens, and gives out a peculiar ammoniacal odour, leaving a minute portion of white ash : it is soluble in solution of pure potassa, and heated with a little nitric acid, affords the fine pink compound above mentioned.

Phosphate of lime calculus is of a pale-brown or grey colour, smooth, and made up of regular and easily separable laminae. It is easily soluble in muriatic acid, and precipitated by pure ammonia, and does not fuse before the blow-pipe. *Calculi from the prostate gland*, are always composed of phosphate of lime.

The ammonio-magnesian, or triple calculus, is generally white, or pale grey, and the surface often presents minute crystals ; its texture is generally compact, and often somewhat hard and translucent ; heated violently by the blow-pipe, it exhales ammonia, and leaves phosphate of magnesia. It is more easily soluble than the preceding ; and oxalate of ammonia forms no precipitate in its muriatic solution.

It frequently happens that calculi consist of a mixture of the two last-mentioned substances, in which case they melt before the blow-pipe, and are hence termed *fusible calculi*. They are white, or nearly so, and softer than the separate substances, often resembling chalk in appearance. They are easily soluble in muriatic acid, and if oxalate of ammonia be added to their solution, the lime is precipitated in the state of oxalate.

Oxalate of lime forms calculi, the exterior colour of which is generally dark-brown, or reddish ; they are commonly rough or tuberculated upon the surface, and have hence been called *mulberry calculi*. Before the blow-pipe, they blacken and swell, leaving a white infusible residue, which is easily recognized as quicklime. Small oxalate of lime calculi are, however, sometimes perfectly smooth upon the surface, and much resemble a hempseed in appearance.

Urate of ammonia I admit among urinary calculi, upon the authority of Dr. Prout, my own experiments having formerly induced me to doubt its existence (*Phil. Trans.* 1808). Its surface is sometimes smooth, sometimes tuberculated ; it is

made up of concentric layers, and its fracture is fine earthy, resembling that of compact limestone ; it is generally of a small size, and rather uncommon, though it often occurs mixed with uric acid. It usually decrepitates before the blow-pipe, is more soluble than the uric calculus, evolves ammonia when heated with solution of potassa, and is readily soluble in the alkaline carbonates, which pure uric acid is not. According to Pfaff, the excrement of the boa constrictor is a suburate of ammonia.

Cystic oxide is a peculiar animal substance ; the calculi composed of it, which are rare, are in appearance most like those of the ammonio-magnesian phosphate. They are soft, and when burned by the blow-pipe, exhale a peculiar fœtid odour. They are soluble in nitric, sulphuric, muriatic, phosphoric, and oxalic acids, and also in alkaline solutions. Cystic oxide forms crystallizable compounds with nitric, muriatic, and oxalic acids. With sulphuric acid it forms a viscid, colourless, and uncrystallizable compound. Analyzed by oxide of copper, M. Lassaigne (*Ann. de Chim. et Phys.*, xxiii., 329) obtained from it

Carbon	36.2
Nitrogen	34.0
Oxygen	17.0
Hydrogen	12.8
					<hr/>
					100

The substances which have been described, with the exception of carbonate of lime and cystic oxide, are sometimes intimately blended in calculi ; sometimes they form alternating layers ; and in a few cases four distinct layers have been observed, the nucleus being uric, upon which the oxalate and phosphate of lime, and the triple phosphate, are distinctly and separately arranged.

Dr. Marcet has described a calculus composed of a peculiar animal matter, which he calls *Xanthic Oxide*, from its property of giving a yellow colour when acted on by nitric acid : he has also announced the existence of calculus composed of *fibrine*. —*Essay on Calculous Disorders*, 2d edit. p. 103.

Dr. Prout and Mr. Smith (*Med. et Chir. Trans.*, xi., 14.) have described calculi composed almost entirely of carbonate of lime ; but this species is exceedingly rare, and among several hundred calculi which I have examined, I never met with it

from the human bladder. Phosphate of lime calculi are small, white, and friable. I have seen many beautiful specimens of carbonate of lime calculus from inferior animals.

Silica, as an ingredient in sand and in some calculi, is very rare. It would appear from the statement of Mr. VENABLES, (*Quart. Journ. N. S.*, December, 1829), that it most commonly is voided in the form of sand. Several supposed cases of silicious sand have been traced to imposture*.

These are the principal chemical facts belonging to the history of urinary calculi. In Dr. Wollaston's valuable papers upon this subject (*Phil. Trans.*, 1797, and 1810), much additional information will be found. In the same work (1806, 1808, and 1810), I have given some account of their peculiarities, depending upon their situation, and have also discussed the operation of solvents, a subject which I have taken up more in detail in the *Quarterly Journal of Science and the Arts*, vol. viii. Dr. Marcet and Dr. Prout have also published excellent dissertations on *Calculous Disorders*, containing all that is most important upon the subject.

Section VII. CUTIS, OR SKIN; MEMBRANE, ETC.

THE skin of animals consists of an exterior albuminous covering, or *cuticle*, under which is a thin stratum of a peculiar substance, called by anatomists *rete mucosum*, and which lies immediately upon the *cutis*, or true skin, of which the principal component is gelatine.

The following are the chemical properties of *pure gelatine*. It is colourless, semi-transparent, and nearly tasteless. It is softened by long-continued immersion in cold water: in hot water it readily dissolves, and forms a solution of a slightly

* Since writing the above, I have seen, in the possession of Dr. Yellowly, what I consider a very unequivocal specimen of silicious calculus: it was taken from a boy by an operation, and consisted chiefly of oxalate of lime, having small cavities in its interior, lined with an apparently chalcedonic crust, which on examination proved to be silicious.

milky appearance, which, if sufficiently concentrated, concretes on cooling into the tremulous mass usually called *jelly*, and which is easily soluble in cold water; when dried in a gentle heat it acquires its original appearance, and is as soluble as before. According to Dr. Bostock, one part of isinglass dissolved in 100 of water, gelatinizes on cooling; but in 150 of water it does not concrete.—(NICHOLSON'S *Journal*, xi. and xiv.) When dry, gelatine undergoes no change, but its solution soon becomes mouldy and putrescent. Submitted to the action of heat, it affords the usual products of animal substances.—(HATCHETT, *Phil. Trans.*, vol. xc.) The relative proportions of its ultimate components, according to Gay-Lussac and Thenard, are

Carbon	47.881
Hydrogen	7.914
Oxygen	27.207
Nitrogen	16.998
					<hr/>
					100

It is readily soluble in diluted acids and alkaline solutions, and forms no soap with the latter.—(HATCHETT, *Phil. Trans.* 1800.) Its aqueous solution is not affected by solution of corrosive sublimate, and few of the metallic salts occasion any precipitate in it. Chlorine passed through its solution occasions a white elastic matter to separate, which is not soluble in water, and which in some properties resembles albumen. It is insoluble in alcohol and ether, but alcohol does not form a precipitate in its aqueous solution. Solution of tannin occasions a white precipitate in solution of gelatine; and hence, vegetable astringents, such as infusion of galls or of oak bark, are generally employed as tests for its presence. But as tannin precipitates albumen, it cannot be relied on as an unequivocal test, unless we previously ascertain the non-existence of albumen by corrosive sublimate.—(BOSTOCK, NICHOLSON'S *Journal*, xiv. and xxi.)

Mr. E. Davy recommends sulphate of platinum as a very delicate test of gelatine, with which it forms a brown insoluble compound, in solutions too weak to be affected by vegetable astringents.—(*Phil. Trans.*, 1820, p. 119.)

The action of sulphuric acid upon gelatine has been investigated by M. Braconnot. Twelve parts of powdered glue and

24 of sulphuric acid were left together for 24 hours; about 60 parts of water were then added, and the whole boiled for 5 hours, adding water at intervals; the solution was then saturated with chalk, filtered, and suffered to evaporate spontaneously. In a month, crystals were deposited, which, being purified by solution and a second crystallization, much resembled sugar of milk, though they differ from that substance in affording a peculiar acid, called by M. Braconnot *Nitrosaccharine acid* when acted upon by nitric acid.—(*Ann. de Ch. et Phys.*, xiii.)

The different kinds of gelatine differ considerably in viscosity. Mr. Hatchett has remarked that the gelatine obtained from skins possesses a degree of viscosity inversely as their softness or flexibility; the most adhesive kinds of gelatine, too, are less easily soluble in water than those which are less tenacious. The principal varieties of gelatine in common use are,

a. Glue, which is prepared from the clippings of hides, hoofs, &c., obtained at the tan-yard; these are first washed in lime-water, and afterwards boiled and skimmed; the whole is then strained through baskets, and gently evaporated to a due consistency; afterwards it is cooled in wooden moulds, cut into slices, and dried upon coarse net-work. Good glue is of a semi-transparent and deep brown colour, and free from clouds and spots. When used it should be broken into pieces, and steeped for about 24 hours in cold water, by which it softens and swells; the soaked pieces may then be melted over a gentle fire, or in a water-bath, and in that state applied to the wood by a stiff brush. Glue will not harden in a freezing temperature, the stiffening depending on the evaporation of its superfluous water.

b. Size is less adhesive than glue, and is obtained from parchment shavings, fish-skin, and several animal membranes. It is employed by bookbinders, paper-hangers, and painters in distemper, and is sometimes mixed with flour, gum, &c.

c. Isinglass is prepared from certain parts of the entrails of several fish; the best is derived from the sturgeon, and is almost exclusively prepared in Russia. It should be free from taste and smell, and entirely soluble in warm water, which is seldom the case, in consequence of the presence of some albuminous parts. When the jelly of isinglass is concentrated by

evaporation and carefully dried, it forms a very choice kind of glue.—AIKIN's *Dictionary*, Art. GELATINE.

Leather is a compound of gelatine and vegetable astringent matter, formed by steeping the skins of animals in the infusions of certain barks. The skins are previously prepared by soaking in lime-water, which renders the cuticle and hair easily separable, and are afterwards softened by allowing them to enter into a degree of putrefaction. In this state they are submitted to the action of infusion of oak-bark, or other astringent vegetable matter, the strength of which is gradually increased until a complete combination has taken place, which is known by the leather being of an uniform brown colour throughout; whereas, in imperfectly tanned leather a white streak is perceptible in the centre.

Tawed leather is made by impregnating the skin duly prepared, with a solution of alum and common salt; it is afterwards trodden in a mixture of yolk of eggs and water.

Curried leather is made by besmearing the skin, or leather, while yet moist, with common oil, which, as the humidity evaporates, penetrates into the pores of the skin, giving it a peculiar suppleness, and making it, to a considerable extent, water-proof. As familiar examples of these processes, the thick sole-leather for shoes and boots is *tanned*; the upper-leather is *tanned* and *curried*; the white leather for gloves is *tawed*; and fine Turkey-leather is *tawed*, and afterwards slightly *tanned*.—AIKIN's *Dictionary*, Art. LEATHER.

The different *membranes* of the body, and the *tendons*, are chiefly composed of gelatine; for by long digestion in warm water they gradually soften, and become ultimately almost perfectly soluble.

Section VIII. MUSCLE, LIGAMENTS, HORN, HAIR, ETC.

WHEN the *muscular parts* of animals are washed repeatedly in cold water, the fibrous matter which remains consists chiefly of albumen, and is in its chemical properties analogous to the clot of blood. Muscles also yield a portion of gelatine; and the flesh of beef, and some other parts of animals, afford a

peculiar substance, of an aromatic flavour, called by Thenard, *osmazome*. Albumen and gelatine constitute the leading nutritive ingredients in the different kinds of flesh used as food, and it is curious that their relative proportions are not very dissimilar in quadrupeds, birds, and fishes, as shown in the following table. The water was determined by evaporation in vacuo, or at a temperature below 212° .

100 parts of Muscle of	Water.	Albumen or fibrine.	Gelatine.	Total of Nutritive Matter.
Beef	74	20	6	26
Veal	75	19	6	25
Mutton	71	22	7	29
Pork	76	19	5	24
Chicken	73	20	7	27
Cod	79	14	7	21
Haddock	82	13	5	18
Sole	79	15	6	21

It is commonly supposed that the flesh of young animals is much more abundant in gelatine than that of old ones, but the fact appears to be that it is merely more soluble and more easily extracted by boiling, and in all cases where it is wished to remove from muscle the whole of the jelly, simmering at a temperature from 100° to 120° should be preferred to boiling, because by a temperature of 212° the albumen is so firmly coagulated as to envelope the gelatine and protect it from the solvent power of the water.

The action of sulphuric acid on muscle has been described by Braconnot : 30 parts of beef fibre, acted on by as much sulphuric acid, yielded a portion of fat, and on diluting the acid mixture, and saturating with chalk, filtering, and evaporating, a substance, tasting like osmazome, was obtained, which was often boiled in different portions of alcohol: the alcoholic solutions, on cooling, deposited a peculiar white pulverulent matter, which Braconnot calls *leucine*, and which, acted upon by nitric acid, affords a crystallizable *nitroleucic acid*.—*Annales de Chimie et Phys.*, xiii., 118. (See *Blood*.)

Ligaments, horn, nail, and feathers, consist principally of albumen.

Hair consists chiefly of a substance having the properties of coagulated albumen. It also contains gelatine, and the soft kind of hair yields it more readily than those which

are harsh, strong, and elastic. (HATCHETT, *Phil. Trans.*, 1800.)

Vauquelin discovered in hair two kinds of oil; the one white, and existing in all hair; the other coloured, yellow from red hair, and dark coloured when obtained from dark hair. Black hair also contains iron and sulphur. He supposes that where hair has become suddenly grey, the effect is produced by the evolution of acid matter, which has destroyed the colour of the oil.

Feathers, quills, and wool, are also possessed of the properties of albumen, and appear to contain very little or no gelatine.

Section IX. FAT, SPERMACETI, ETC.

THE fat of animals, when freed by fusion or pressure from cellular membrane, is of various degrees of consistency, as seen in *tallow*, *lard*, and *oil*. When pure, it has little taste or smell, but it acquires both by keeping, and becomes rancid and slightly sour. The softer varieties fuse at about 90° , and the harder at about 120° . Decomposed at a red heat, they afford abundance of olefiant gas, and a small portion of charcoal; products analogous to those of vegetable oil. When burned, they produce water and carbonic acid, containing, when pure, the same ultimate elements, in the same proportions as vegetable oils.

Nitric acid, heated in small quantity with any of the fatty substances, renders them harder, and considerably increases their solubility in alcohol. Among the vegetable oils this change is most remarkably produced upon cocoa-nut and castor-oils, the latter becoming converted into a solid matter, which, when cleansed of adhering acid by washing, somewhat resembles soft wax.

The experiments of Braconnot and Chevreul, already quoted, have shown that the different kinds of oil and fat contain two substances, to which they have given the names *stearine* and *elaine*, the former solid, the latter liquid at common temperatures. The following table shows their relative proportions in different fats and oils:

	Elaine.	Stearine.
Butter, made in summer	60	40
Ditto, winter	37	63
Hogs'-lard	62	38
Beef-marrow	24	76
Mutton-marrow	74	26
Goose-fat	68	32
Ducks'-fat	72	28
Turkeys'-fat	74	26
Olive-oil	72	28
Almond-oil	76	24

These principles may be obtained by boiling hogs'-lard in alcohol; the fluid, on cooling, deposits a concrete matter, which is to be purified by a second solution; it is then pure *stearine*, white, brittle, tasteless, and inodorous; it fuses at a little below 120° , and forms soap with alkalis.

When the alcohol which has deposited the whole of the stearine is distilled, an oily liquid remains, which is *elaine*. It is fluid at 58° ; it generally is of a yellow colour, and is convertible into soap.

When soap composed of hogs'-lard and potassa is put into water, a portion only is dissolved; the remainder consists of white scales, composed of the alkali united to a peculiar acid, called by Chevreul, from its pearly appearance, *margaritic* or *margaric acid*, and separable from the above combination by muriatic acid.

It is insoluble in water, tasteless, fusible at 134° , and crystallizes, on cooling, in brilliant white needles. It is soluble in alcohol. It unites with potassa in two proportions, the one compound, containing 100 acid + 8.80 potassa; the other, 100 acid + 17.77 potassa. These compounds have been termed *margarates of potassa*.

The portion of the hogs'-lard soap soluble in water, consists of another peculiar substance united to potassa, which Chevreul has called *oleic acid*. It may be obtained from its solution by tartaric acid, which causes it to separate in the form of an oily matter, that is to be again united to potassa, and separated as before. This substance solidifies at about 40° , and it forms compounds, called *oleates*. It appears probable that, by the action of alkalis, the stearine is converted into margaric acid, and the elaine into oleic acid.—*Ann. de Chim.*, xciv.

By mixing 1 volume of carbonic acid with 10 of carburetted

hydrogen, and 30 of hydrogen, and passing the mixture through a red-hot porcelain tube, Berard is said to have produced a substance in small white crystals, having many of the properties of fat.—THOMSON'S *Annals*, xii. By igniting a mixture of coal-gas and steam, Doberëiner is also said to have obtained a somewhat similar compound.

Spermaceti or *Cetine* is a peculiar matter, which concretes from the oil of the *spermaceti whale*. It fuses at 112° , and at higher temperatures is volatile; but, if repeatedly distilled, it loses its solid form, and becomes a liquid oil. It is soluble in boiling alcohol, and abundantly so in ether. It forms a soap with potassa, which yields, on decomposition, by an acid, a substance formerly called by Chevreul, *cetic acid*.—*Ann. de Chim.*, xcv. This appears to be the same substance which he has more lately called *ethal*: it is more soluble in alcohol than spermaceti, and combines with bases into soapy compounds. Subjected to destructive distillation, spermaceti yields a large proportion of olefiant gas.

Spermaceti Oil consists, according to Dr. Ure, of

Carbon	.	.	.	10 atoms	78.00
Hydrogen	.	.	.	9 „	11.80
Oxygen	.	.	.	1 „	10.20
					<hr/>
					100

In the oil of the sea-hog (*Delphinus Phocæna*) Chevreul found a peculiar substance, which he calls *phocenine*, and which is converted by saponification into *phocenic acid*. He obtained it by shaking the oil with hot alcohol, and allowing the mixture to stand for twenty-four hours. The lighter portion is then decanted off and distilled: it leaves an oily matter, which, by the action of cold and weak alcohol, yields phocenine. It remains fluid at 0° , has a slight odour, does not redden litmus, and dissolves in alcohol.

In the *yolk of eggs* there is a considerable quantity of oily matter, which may be obtained by pressure after boiling; it is yellow and tasteless. The yolk also contains phosphorus, which, when the dry yolk is burnt, becomes phosphoric acid, and defends the charcoal from combustion by the glazing which it forms. (PROUT, *Phil. Trans.*, 1822.)

Ambergris, which is a concretion from the intestines of the spermaceti whale, also contains a considerable portion of fatty

matter, amounting, in some specimens, to 60 *per cent.*, which, according to Chevreul, resembles cholesterine. Pelletier and Caventou have given it the name of *ambreine*, and it is stated to be convertible by nitric acid, into a peculiar body, which they have called *ambreic acid*. It is only found in the unhealthy animal.—(HOME's *Lectures on Comparative Anatomy*, vol. i., p. 470.) Benzoic acid has been found in some specimens of ambergris; in others, equally genuine, there are no traces of it.

Intestinal concretions sometimes bear a close resemblance to gall stones, but they often contain peculiar substances or are formed upon extraneous nuclei. Dr. Ure has described one resembling ambergris. (DICT. ART. INTESTINAL CONCRETIONS.) These concretions are not uncommonly formed upon fruit stones, and seem to be peculiarly frequent where the diet has consisted of oatmeal. One examined by Mr. Children (*Phil. Trans.*, 1822) consisted of,

Animal matter, chiefly gelatine	. . .	25.20
Resin	. . .	3.90
Ammonio-magnesian phosphate	. . .	5.16
Phosphate of Lime	. . .	45.34
Vegetable fibre	. . .	20.30
		<hr/> 99.90

Alvine calculi have sometimes a peculiar softness upon the surface resembling velvet. One of these was found by Dr. Wollaston to consist of extremely minute vegetable fibres, or short needles, pointed at both ends; which he immediately conjectured to arise from some kind of food. For some time, however, he failed in his attempts to trace this substance to its origin: but Mr. Clift, of the College of Surgeons, to whom the subject was mentioned in conversation, having put the question, whether this fibrous substance might not proceed from oats, Dr. Wollaston was induced to examine the structure of this seed; and the result fully verified Mr. Clift's conjecture.

In Dr. Alexander Monro's "Morbidity Anatomy of the Gullet," mention is made of forty-two alvine concretions collected by the author's father, which were examined by Dr. Thomson. Their structure (with one exception, similar in all) is described by Dr. Monro "as more or less porous, and somewhat like to dried sponge, and when examined by the aid of a mag-

nifying-glass, seems to be made up of a number of very small fibres intimately interwoven with each other, like those in a hat, or in chamois leather; and the interstices between the fibres are filled up with earthy matter." And he adds, "in the centre of the concretion, a *prune* or a *cherry stone*, or a small piece of bone, or a biliary calculus, is generally found."

The *brain of animals*, when boiled in alcohol, furnishes a peculiar fatty matter, which the solution deposits as it cools, in brilliant scales. It requires a higher temperature than that of boiling water for its fusion, and appears, in many respects, analogous to cholesterine. The same substance is often seen in the alcohol employed to preserve anatomical preparations of the brain and nerves.

According to Vauquelin, the *cerebral substance* consists of

Water	80.00
White fatty matter	4.53
Red fatty matter	0.70
Albumen	7.00
Osmazome	1.12
Phosphorus	1.50
Acids, salts, and sulphur	5.15
	<hr/>
	100

The *pulp of nerves* seems to be of a similar nature.—(THOMSON'S *System*, vol. iv., p. 482.)

Cantharadin is a term which has been applied to the active principle of the Spanish fly (*Lytta vesicatoria*). If the watery extract of these insects be digested in alcohol, a tincture is obtained, which by slow evaporation yields a resinous residue; if this be digested in ether, it forms a yellow solution; by spontaneous evaporation it deposits crystalline plates, which may be freed from some adhering colour by alcohol; they resemble spermaceti in appearance, and are soluble in boiling alcohol, but precipitate as it cools. They are insoluble in water. Besides this peculiar principle, cantharides contain a green inert oil, soluble in alcohol; a black matter, insoluble in alcohol, but soluble in water; a yellow substance, soluble in both; a considerable portion of uric acid; a little acetic acid, and phosphates of lime and magnesia.

Section X. SHELL AND BONE.

WE are indebted to Mr. Hatchett for two excellent dissertations on the chemical properties of these parts of animals, published in the *Philosophical Transactions* for 1799 and 1800.

He has divided *shells* into two classes; the texture of the first is compact, brittle, and resembling porcelain; their surface is smooth, and they are often beautifully variegated. When exposed to a red heat they crackle, and lose the colour of their enamelled surface, emitting scarcely any smoke or smell. They dissolve in dilute muriatic acid with copious effervescence, and form a transparent solution, in which neither pure ammonia nor acetate of lead produce any precipitate, but carbonate of ammonia throws down carbonate of lime. Hence these, which are called *porcellaneous shells*, may be considered as composed of carbonate of lime, united to a very small portion of gelatine: most of the univalve shells, such as whelks, limpets, cowries, and many of the beautiful convoluted shells of tropical countries, belong to this class.

The second class, or *mother-of-pearl shells*, are tougher, glossy, and iridescent; they are mostly bivalves, and all the oyster and muscle species belong to it. When heated, they exhale smoke and the smell of burned horn; immersed in muriatic acid, they only partially dissolve, and leave a series of cartilaginous layers, and an outer epidermis. Each membrane appears to have a corresponding stratum of carbonate of lime, the solution indicating no trace of any phosphate. The animal part is in some cases, as in mother-of-pearl, tough and indurated, and when dried becomes exactly like horn; in other instances, as in the bone of the cuttle-fish, it appears in the form of delicate and tender membrane.

In both classes of shells, therefore, the hardening principle is carbonate of lime; in porcellaneous shells there is very little animal matter, which is gelatine; and in mother-of-pearl shells, it is albumen, and in larger quantities.

Pearls are exactly similar in composition to what is termed *mother-of-pearl*, in which Mr. Hatchett found

Carbonate of lime	66
Albumen	24
					<hr/>
					100

In the *scales of fish*, and in the *crusts* of lobsters, crabs, prawns, and cray-fish, Mr. Hatchett found the animal portion to consist of cartilage: the hardening part was a mixture of carbonate and phosphate of lime. From *lobster-shell* Merat-Guillot obtained

Carbonate of lime	60
Phosphate of lime	14
Cartilage	26
					<hr/>
					100

Vauquelin obtained from 100 parts of *hen's egg-shell*,

Carbonate of lime	89.6
Phosphate of lime	5.7
Animal matter	4.7
					<hr/>
					100

Zoophytes, according to Mr. Hatchett's researches, may be divided into four classes; the first class resembles porcellaneous shells; they consist entirely of carbonate of lime, with a very minute quantity of gelatinous matter; of this the common white coral (*madrepora virginea*) is an example. The second consists of carbonate of lime, and a cartilaginous substance, and are therefore analogous to mother-of-pearl shell; to this class belong the *madrepora ramea*, and *madrepora fascicularis*. The third class is composed of a cartilaginous matter, with carbonate and phosphate of lime; to this belongs the red coral (*gorgonia nobilis*). The fourth class contains sponges, composed almost entirely of albuminous matter.—(*Phil. Trans.*, 1800.)

Bone and *Ivory*, like the preceding substances, are essentially composed of soft and hard parts. When ground bone is digested in warm water, a portion of fat is first separated, and by long-continued ebullition, a solution which gelatinizes on cooling is obtained. If fresh bone be immersed in diluted muriatic acid, the fat, gelatine, and hardened matter are dissolved, and a kind of skeleton of the bone remains in the form

of a cartilaginous substance, which when dried, exactly resembles horn. It appears, therefore, that the soft parts of bone are, *fat*, *gelatine*, and *albumen*.

The earthy salts, which constitute the hardening principle of bone, are phosphate and carbonate of lime, with a minute quantity of sulphate of lime, and traces of phosphate of magnesia. Fourcroy and Vauquelin obtained from ox-bones,

Animal matter	51.0
Phosphate of lime	37.7
Carbonate of lime	10.0
Phosphate of magnesia	1.3
	<hr/>
	100

The *enamel of teeth* is perfectly destitute of cartilage, and consists chiefly of phosphate of lime and a portion of gelatine. Mr. Pepys found its component parts,

Phosphate of lime	73
Carbonate of lime	6
Gelatine	16
	<hr/>
	100

The same chemist has given the following as the composition of the teeth (Fox, *On the Teeth*) :

	Roots of the Teeth.	Teeth of Adults.	First Teeth of Children.
Phosphate of lime	58	64	62
Carbonate of lime	4	6	6
Cartilage	28	20	20
Loss	10	10	12
	<hr/>	<hr/>	<hr/>
	100	100	100

When bones are submitted to destructive distillation, the gelatine and albumen which they contain is abundantly productive of ammonia; water and carbonic acid are also formed, and a portion of highly fœtid empyreumatic oil. There remains in the vessel a quantity of charcoal mixed with the earthy substances, which is, in that state, called *ivory black*. It is employed as the basis of some black paints and varnishes, and is applicable to many other useful purposes in the arts, as a variety of animal charcoal.

Section XI. OF ANIMAL FUNCTIONS.

CHEMISTRY has hitherto done little towards elucidating the functions of animals, and it is scarcely possible to describe the little that has been done, without such frequent reference to anatomical and physiological inquiries as would be irrelevant to the present work; I shall, therefore, only enumerate the principal chemical phenomena that have been experimentally illustrated, in relation to this subject.

Digestion is a process by which the food of animals is converted into chyle, and which, in conjunction with *respiration*, tends to the production of blood. The mechanism by which it is carried on differs considerably in the different classes of animals: the present remarks will relate chiefly to man, and to the carnivorous tribe.

The food, duly masticated in the mouth, and blended with a considerable portion of saliva, is propelled into the stomach, where it soon undergoes a remarkable change, and, in the course of a few hours, is converted into an apparently homogeneous pulpy mass, which has been termed *chyme*, and which has little or no resemblance to the original food. This very curious change is only referable to the operation of a secretion peculiar to certain glands of the stomach; it has been termed *gastric juice*, and all that is known respecting it, is, that it has very energetic solvent powers, in regard to the greater number of animal and vegetable bodies; the remarkable property of living substances to resist its action is curiously illustrated by the circumstance that the stomach itself, after death, is occasionally eaten into holes by its action; it instantly coagulates all albuminous substances, and afterwards softens and dissolves the coagulum. There are some substances that remarkably resist its action, such as the husk of grain, and of many seeds, which, if not previously broken by mastication, pass through the stomach and bowels nearly unaltered. It is hardly worth while to detail the experiments that have been undertaken on the gastric juice, since they are much at variance, and it is impossible to say whether the secretion has ever been examined in a state even approaching to purity. It has been described as a glairy fluid, of a saline taste; sometimes it is said to be

acid, and sometimes bitter ; but no light whatever has been thrown by any of these researches upon the cause of its singular solvent energies.

It has sometimes been matter of surprise, that although animals drink copiously with their food, the consistency of the chyme is not affected by it, and by the time that it reaches the right, or pyloric extremity of the stomach, the liquid has disappeared. Sir Everard Home's curious physiological researches have shewn that liquids are copiously and rapidly removed by absorbents belonging principally to the left, or cardiac portion of the stomach, and that during digestion there is an imperfect division of the stomach into two cavities, by the contraction of the bands of muscular fibres about its centre. He has also shewn that these liquids very soon reach the kidneys, and pass off by urine ; and was led to believe that the spleen was the channel of communication ; an opinion, however, which his subsequent researches tended to disprove.—(*Lectures on Comparative Anatomy*, p. 221.)

The chyme passes from the stomach into the small intestines, where it soon changes considerably in appearance ; it becomes blended with bile, and is separated into two portions, one of which is white as milk, and is termed *chyle** ; the other passes on to the large intestines, and is ultimately voided as excrementitious. The chyle is absorbed by the *lacteals*, which terminate in the common trunk, called the *thoracic duct* ; it is there mixed with variable proportions of lymph, and poured into the venous system.

The *excrements of animals* have been examined by Berzelius (*GEULEN'S Journal*, vi. ;) by Vauquelin (*Annales de Chimie*, xxix.) ; and by Thaer and Einhoff. An abstract of these experiments has been published by Dr. Thomson, in the 4th volume of his *System of Chemistry*.

Chyle has been examined by several chemists, and their results are not widely different. During some physiological

* The necessity of bile to the formation of chyle has been further illustrated by Mr. Brodie (*Quarterly Journal*, O. S., xiv. 341). When the choledoch duct was tied so as effectually to prevent the flow of bile into the intestine, no chyle was formed ; the chyme appeared little altered, and the lacteals, instead of their usual milky fluid, contained a transparent fluid ; consisting, apparently, of lymph, and of the more fluid part of the chyme.

researches in which I assisted Mr. Brodie, I had an opportunity of collecting it in considerable quantities in several carnivorous and graminivorous animals, and presented an account of my experiments upon it to the Royal Society.—(*Phil. Trans.*, 1812, p. 91.)

Chyle is an opaque white fluid, having a sweetish saline taste; its specific gravity is inferior to that of the blood. It exhibits slight traces of alkaline matter when tested by infusion of violets; soon after removal from the thoracic duct, it gelatinizes spontaneously, and afterwards gradually separates into a firm yellowish-white coagulum, and a transparent colourless serum; so that, like the blood, it enjoys the property of spontaneous coagulation.

The *coagulum of chyle* possesses properties closely resembling those of the caseous portion of milk, and may hence be considered as a variety of albumen; the *serum of the chyle*, when heated, deposits a few flakes of albumen, and by evaporation to dryness affords a small proportion of a substance analogous to sugar of milk. Small portions of phosphate of lime, carbonate of soda, and common salt, may also be detected in the chyle. In these experiments I found no distinctive difference in the chyle of graminivorous and carnivorous animals; I examined it from the horse, the ass, the dog, and the cat; Dr. Marcet thinks that the former is less abundant in albumen than the latter*. (THOMSON'S *Annals*, vol. vii.) From a comparative analysis of the chyle of two dogs, by Dr. Prout, of which one was fed on vegetable, and the other on animal food, the components were found to be as follow (*Ann. of Phil.*, xiii. 25):—

	Vegetable Food.	Animal Food.
Water	93.6	89.2
Fibrine	0.6	0.8
Incipient albumen?	4.6	4.7
Albumen with a little red colouring matter	0.4	4.6
Sugar of milk	a trace	0.0
Oily Matter	a trace	a trace
Saline Matter	0.8	0.7
	<hr/> 100	<hr/> 100

* It is a curious question, whence the nitrogen, which constitutes an abundant ultimate principle of the chyle of herbivorous animals, is derived; we find it in very small proportion only in their ordinary food, and yet I could discern no difference in the composition of the albuminous portion of their chyle, and that of animals fed exclusively on meat.

There can be little doubt that the bile performs an important part in the change which the chyme suffers in the small intestines; it has been conjectured that its aqueous, and perhaps its alkaline, parts, are employed as components of chyle, while the albumino-resinous matter combines with the excrementitious portion, and tends to stimulate the intestinal canal towards promoting its propulsion. Whether the bile is absolutely necessary to the formation of chyle, is a question that has not been satisfactorily answered; but its importance is demonstrated by the emaciation that attends its deficiency, and by the disordered state of bowels that accompanies its imperfect secretion. Sir Everard Home, in his *Lecture on the Functions of the Lower Intestines*, (*Lectures*, p. 468,) has offered some curious facts connected with this subject, to which I refer the physiological reader. He is of opinion that, in the large intestines, a portion of the food unfit for chyfication is, by a process not widely different from that above described, converted into fat, which is afterwards absorbed and conveyed to different parts of the body.

In chyle we cannot fail to observe a close approximation to blood; it is deficient only in colouring matter, and the albumen which it contains differs a little from that existing in the blood itself; it appears, therefore, that the albumen is perfected, and the colouring matter formed, in the process of circulation; the saccharine principle of the chyle is also no longer perceptible.

The difference between arterial and venous blood has been adverted to in a previous section; the former is of a florid red colour, and circulates in the arterial system; it is contained in the left ventricle of the heart, and thence carried by the *aorta*, and its ramifications, to every part of the body, tending to reproduction and secretion: it afterwards enters the veins which arise from the extremities of the arteries, and form accompanying branches and trunks ultimately uniting in the *venæ cavæ*, which pour their contents into the right auricle of the heart; the venous blood is thence propelled into the right ventricle, from which the pulmonary artery arises, transmitting it through the lungs, whence it is returned by the pulmonary vein into the left auricle, which transmits it to the left ventricle, from which issues the *aorta* as aforesaid. So that the right cavities of the heart receive venous blood, and transmit it through the

lungs, whence it returns to the left side of the heart, in the arterial state. In the lungs the blood is infinitely subdivided, and spread over a very large surface in vessels so delicate as to admit of the operation of the atmospheric air contained in their cells ; it enters the pulmonary structure in the *venous* state by the *pulmonary artery*, and returns in the *arterial* or *aërated* state, by the *pulmonary vein*. It now remains to examine the changes which the blood undergoes during pulmonary circulation.

Respiration is the process of receiving a quantity of air into the lungs, whence, after having been retained a short time, it is again expelled in the action of expiration : and, if now examined, a portion of its oxygen is found converted into carbonic acid, and it is more or less loaded with aqueous vapour. The nitrogen of the air probably remains quite passive, although from Dr. Edwards's experiments there appears to be some doubt upon this subject, for sometimes it appeared to be emitted, and sometimes absorbed in small quantities by the blood.

Obvious circumstances render it very difficult to ascertain the quantity of air taken into the lungs at each natural inspiration, as well as the number of respirations made in a given time ; the former is perhaps about 15 or 16 cubic inches, and the latter about 20 in a minute.

It has been by some supposed that the air suffers an absolute diminution of bulk, but the experiments that have been adduced to prove this, can, I think, scarcely be regarded as satisfactory ; it seems, on the contrary, most probable that the volume of air expired is exactly equal to that inspired, and consequently the only chemical change that is evident is the saturation of a portion of its oxygen with carbon*. The quantity of carbonic acid emitted at each expiration, varies at different periods of the day, and probably also in different individuals ; it appears at its maximum during digestion, and at its minimum in the morning, when the stomach is empty, and when no chyle is flowing into the blood. Dr. Prout has shown that fermented liquors and vegetable diet diminish the proportion of carbonic acid, and that the same thing happens when

* Dr. Edwards thinks that a portion of air disappears, but that it is very variable in its amount.—(Bosrock, *Physiology*, ii., 101.)

the system is affected by mercury. (THOMSON'S *System*, iv., 621.)

The air expired after a single expiration has generally been regarded as containing, on an average, 3.5 *per cent.* of carbonic acid; Messrs. Allen and Pepys, however, in their valuable *Essay on Respiration* (*Phil. Trans.*, 1808), have estimated it at about twice that quantity; it amounted, in their experiments, to 27.5 cubic inches per minute, a considerable quantity when we reflect upon the comparative proportion of carbon existing in our food, and the other means of escape which it has from the body. Dr. Prout estimates the carbonic acid at 8 *per cent.*

The aqueous vapour contained in the expired air is probably entirely secreted by the exhalents distributed over the surface of the air-vessels of the lungs; attempts have been made to estimate its quantity, but without success; perhaps the nearest estimate is about 3 grains per minute; it is liable to variation, and can scarcely be considered as a product of respiration.

It has been above stated that the whole of the venous blood is propelled through the vessels of the lungs, where it is subjected to the action of the air; the chyle is of course carried along with it, and when it returns by the pulmonary vein to the left side of the heart, it has undergone a considerable change in appearance, having lost its dingy colour, and acquired a fine florid red; the chyle also has become perfect blood. The change of colour is evidently owing to the action of the air, which takes place through the thin coats of the circulating vessels, and the end thus attained is the removal of the carbon from the venous blood, by which the colouring matter was obscured; the carbon to be thus readily soluble in oxygen must be in some peculiar state; a portion of it is also removed by the absorbents, and transferred to the glands situate at the root of the lungs, between the subdivisions of the bronchiæ, which often contain a large portion of black matter. This has sometimes been referred to soot inhaled with the air, but many circumstances render it more probable that it is a carbonaceous deposit from the blood. The only chemical difference, then, which can be satisfactorily detected between arterial and venous blood, is the existence of a certain excess of carbon in the latter, which it gives off to oxygen, forming carbonic acid;

the blood is thus fitted for the renovation of parts, for the formation of secretions, and for the sustenance of life by its action on the cerebral system ; for although the heart does not directly refuse to circulate venous blood, paralysis and torpor ensue when blood, not aërated, passes into the vessels of the brain.

It has already been shown that the blood suffers very important changes in the kidneys and liver ; the function of *perspiration* also must be considered as connected with an alteration of the circulating fluid, for moisture, carbonic acid, and minute quantities of phosphoric acid, and saline matter, among which is common salt, are evacuated by the cutaneous vessels. This quantity of humidity is sometimes very considerable, especially during violent exercise in warm weather, and it probably contributes materially to diminish the temperature of the body ; a portion of water, however, is at all times passing off by the skin, as may be seen by putting the hand into a dry and cold glass, which soon becomes dimmed by the condensation of vapour.

Different animals require very different quantities of oxygen for the purposes of respiration. Man, and warm-blooded animals, consume the largest quantity ; the amphibious tribes not only require less, but can breathe in an atmosphere which will not support the life of the former ; and many insects take such small quantity, as sometimes to have been supposed capable of living without air, which is not the case. In the production of carbonic acid, all animals agree ; and, consequently, the nature of the deterioration suffered by the air, is similar throughout the animal creation.

Fishes breathe the air which is dissolved in water ; they therefore soon deprive it of its oxygen, the place of which is supplied by carbonic acid ; this is in many instances decomposed by aquatic vegetables, which restore oxygen, and absorb the carbon ; hence the advantage of cultivating growing vegetables in artificial fish-ponds. It has been ascertained by Biot, and verified by others, that the air-bladders of fish that live in very deep water, are filled with a mixture of oxygen and nitrogen, in which the former greatly preponderates ; but in fish that are taken near the surface, the nitrogen is most abundant. In the *trygla lyra*, always caught in very deep water, the air-bladder contained 87 *per cent.* of oxygen : in the carp and

roach, according to Fourcroy and Priestley, the air-bladder contains little else than nitrogen.—(BIOT, *Mémoires d'Arcueil*, i. and ii.)

The production of *animal heat* is perhaps the most recondite of all the functions; the power appears to belong to all animals, though to some in a very inferior degree. The higher orders of animals always maintain a temperature of about 100° ; it varies a little in different parts of the body, the extremities and surface being a degree or two colder than the interior vital organs. This temperature is probably very little affected by external circumstances, a hot or cold atmosphere producing no corresponding change in the heat of the circulating blood.

When the chemical changes that take place during respiration had been inquired into, and when it was found that the capacity of carbonic acid for heat was less than that of oxygen, it was supposed that the conversion of oxygen into carbonic acid was the cause of the rise of temperature: and as the heat of the lungs does not exceed that of other parts, it was asserted that the air was absorbed by the blood, and that the production of carbonic acid, and consequent evolution of heat, took place gradually during the circulation. To these opinions many strong objections have from time to time been urged by different physiologists, but their complete subversion followed the researches of Mr. Brodie (*Phil. Trans.*, 1812), who found that the heart was capable of retaining its functions for some hours, and of carrying on circulation in a decapitated animal, and consequently independent of the influence of the brain, when respiration was artificially carried on. Under these circumstances it was observed, that although the change of blood from the venous to the arterial state was perfect, no heat was generated, and the animal cooled regularly and gradually down to the atmospheric standard. In more than one instance I examined, at his request, the expired air, and found that it contained as much carbonic acid as was produced by the healthy animal; so that here, circulation went on, there was the change of oxygen into carbonic acid, and the alteration of colour in the blood, and yet no heat whatever appeared to be generated.

In these cases, a period was also put to the secretory functions; and it has been observed by other physiologists, that if the nerves that supply any of the glands are injured or divided,

there is a corresponding change or suspension of their secretion. Electricity has sometimes been supposed to have some connexion with the nervous influence, and the fact of some of the secretions being alkaline, while others are acid (corresponding to negative and positive influence), has been adduced in favour of the supposition*; but experiment has gone little way to sanction such a notion; and although it has been proved that the nervous influence contributes to the generation of heat in animals,—that it presides over the phenomena of secretion, as well as of voluntary motion,—the actual cause of this influence or energy remains among those mysteries of nature which, doubtless, for the wisest purposes, are hidden to the human understanding.

* In the *Philosophical Transactions* for 1809, p. 385, Sir Everard Home has given an account of these views, in a paper entitled *Hints on the Subject of Animal Secretions*.

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